Bright and dark exciton transfer in quantum dot arrays

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Collaboration and publications:

[1] A. N. Poddubny, A. V. Rodina, Nonradiative and radiative Förster energy transfer between quantum dots, JETP. **122**, 531 (2016).

[2] F. Liu, A. Rodina, D.R. Yakovlev, A.A. Golovatenko, A. Greilich, E.D. Vakhtin, A. Susha, A.L. Rogach, Yu.G. Kusrayev, and M. Bayer, Magnetic field enhancement of Foerster energy transfer in ensemble of colloidal CdTe nanocrystals. Phys. Rev. B **92**, 125403 (2015).

[3] A.A. Golovatenko, M.A. Semina, A.V. Rodina, T.V. Shubina. Density of states and photoluminescence spectra in the dense arrays of CdSe/ZnSe quantum dots with Gaussian potential profile. – Acta Physica Polonica A **129**, 107 (2016).

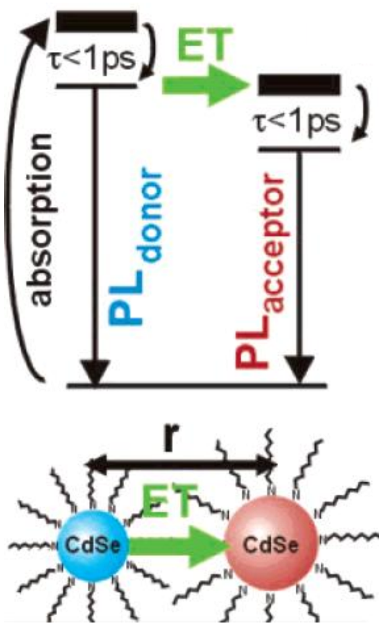
[4] Shubina,TV; Rodina,AV; Semina,MA; Golovatenko,AA; Toropov,AA; Rakhlin,MV; Sedova,IV; Sorokin,SV; Gronin,SV; Sitnikova,AA; Kuritsyn,DI; Sergeev,SM; Krasil`nik,ZF; Ivanov,SV. Spectral selection of excitonic transitions in a dense array of CdSe/ZnSe quantum dots. Phys. Status Solidi B 253, 1485 (2016).

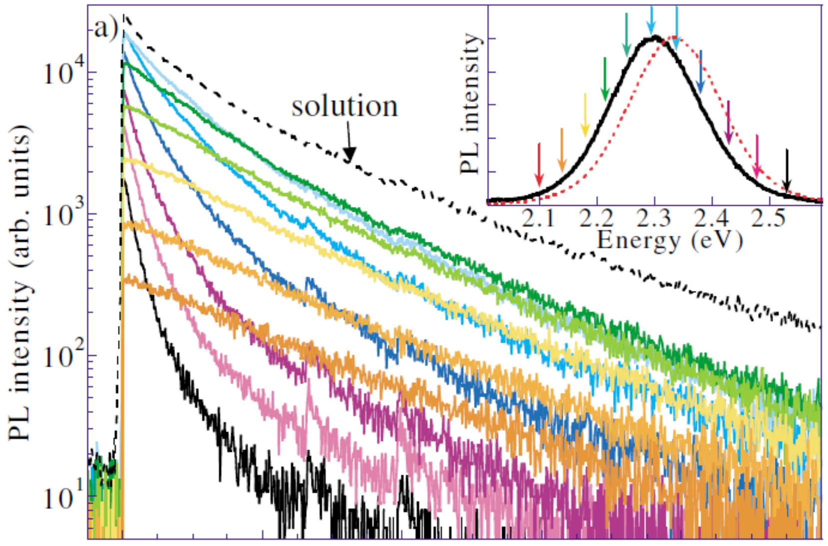
[5] TV Shubina, MA Semina, KG Belyaev, AV Rodina, AA Toropov, SV Ivanov, Förster Resonance Energy Transfer and Harvesting in II–VI Fractional Monolayer Structures, Journal of Electronic Materials, 1-5 (2016).

[6] TV Shubina, KG Belyaev, MA Semina, AV Rodina, AA Golovatenko, AA Toropov, SV Sorokin, IV Sedova, V Yu Davydov, AN Smirnov, PS Kop'ev, SV Ivanov. Resonance energy transfer in a dense array of II–VI quantum dots. Physics of the Solid State 58, 2256-2260 (2016).

The work was supported by Russian Science Foundation (Project number 14-22-00107)

Förster Resonant Energy Transfer (FRET)





CdSe

T=300 K

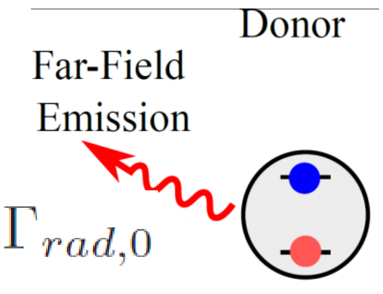
S. A. Crooker et al, PRL (2002)
M. Achermann et al, J. Phys. Chem B (2003)
M. Furis et al, JPC B (2005)

Dipole-Dipole Interaction:

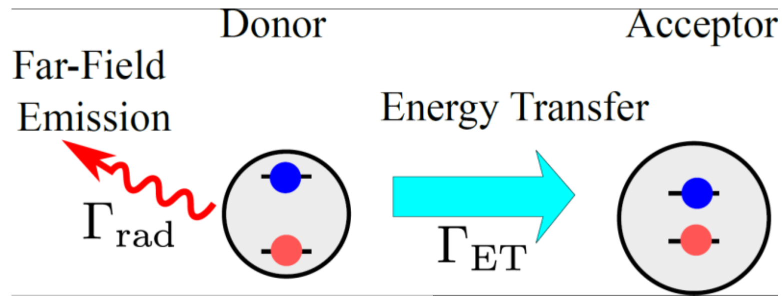
$$\boxed{\Gamma_{\mathrm{ET}} \propto \frac{d_{\mathrm{D}}^2 d_{\mathrm{A}}^2}{r^6}\Theta}$$

T. Forster, Naturwissenschaften **33**, 166 (1946)

Questions:



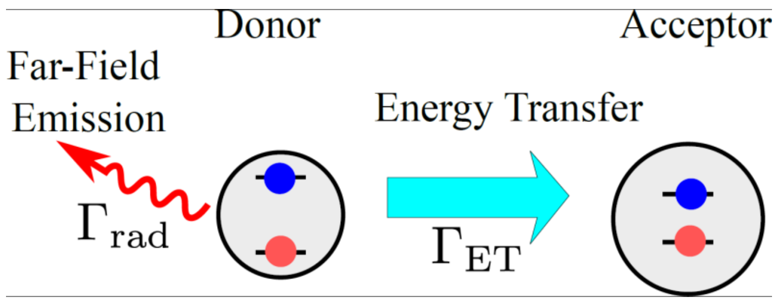
$$\frac{1}{\tau_{D,0}} = \Gamma_{rad,0}$$



$$\frac{1}{\tau_D} = \Gamma_{rad,0} + \Gamma_D$$

- How to determine energy transfer (ET) rate experimentally ?
- How to distinguish between non radiative (Förster ET) and radiative (Purcell, reabsorption) effects ? $\boxed{\Gamma_D = \Gamma_{ET} + \Delta\Gamma_{rad}}$
- How does FRET work at low temperatures when mostly the dark (dipole-forbidden) exciton is populated ?
  Can the dark exciton participate in FRET ?

[1] A. N. Poddubny, A. V. Rodina, Nonradiative and radiative Förster energy transfer between quantum dots, JETP. **122**, 531 (2016).



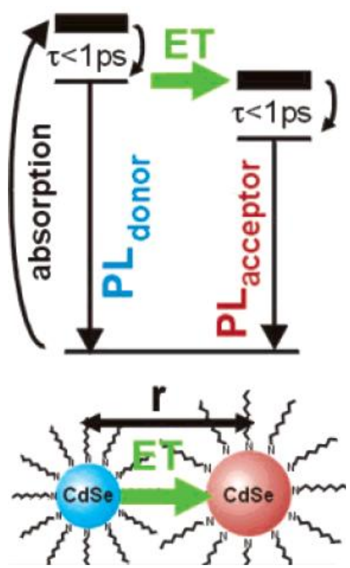
$\mathbf{d}_D \quad E_D = \hbar\omega_D \qquad \mathbf{d}_A \quad E_A = \hbar\omega_A$

$$\frac{1}{\tau_D} = \Gamma_{rad,0} + \Gamma_D$$

$$\Gamma_D = \Gamma_{ET} + \Delta\Gamma_{rad}$$

Non radiative life time: $\tau_A = 1/(2\gamma_A)$

N_D



N_A

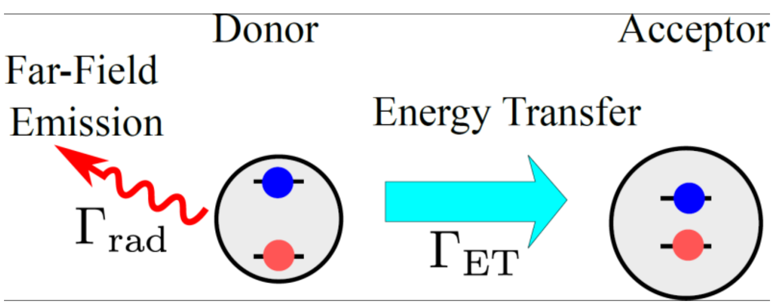
$N_{A,0}$

$$\frac{dN_{\rm D}}{dt} = -\left(\Gamma_{\rm rad,0} + \Gamma_{\rm D}\right) N_{\rm D} + G$$

$$\frac{dN_{\rm A}}{dt} = -\frac{N_{\rm A}}{\tau_{\rm A}} + \Gamma_{\rm ET} N_{\rm D}\,,$$

$$\frac{dN_{\rm A,0}}{dt} = -\frac{N_{\rm A,0}}{\tau_{\rm A,0}} + \frac{N_{\rm A}}{\tau_{\rm A}}\,.$$

[1] A. N. Poddubny, A. V. Rodina, Nonradiative and radiative Förster energy transfer between quantum dots, JETP. **122**, 531 (2016).



$$\frac{1}{\tau_D} = \Gamma_{rad,0} + \Gamma_D$$

$$\Gamma_D = \Gamma_{ET} + \Delta\Gamma_{rad}$$

Non radiative life time: $\tau_A = 1/(2\gamma_A)$

$\mathbf{d}_D \quad E_D = \hbar\omega_D \qquad \mathbf{d}_A \quad E_A = \hbar\omega_A$

ET rate: $$\boxed{\Gamma_{\mathrm{ET}} = \frac{2\pi}{\hbar}\Theta|\boldsymbol{d}_{\mathrm{D}} \cdot \hat{G}\boldsymbol{d}_{\mathrm{A}}|^2}$$

$$\Theta = \frac{1}{\pi\hbar}\frac{\gamma_A}{(\omega_A - \omega_D)^2 + \gamma_A^2}$$

Electrostatic approximation: $$G_{0,\alpha\beta} = \frac{3r_\alpha r_\beta - r^2\delta_{\alpha\beta}}{\varepsilon r^5} \qquad qr \ll 1$$

Account of retardation: $$G_{\alpha\beta} = \left(\delta_{\alpha\beta} + \frac{1}{q^2}\frac{\partial^2}{\partial x_\alpha \partial x_\beta}\right)\frac{e^{iqr}}{\varepsilon r} \qquad q = \omega_D\sqrt{\varepsilon}/c$$

Local field effect: $\mathbf{d}_{D,A} \to \mathbf{d}_{D,A} 3\varepsilon_{QD}/(\varepsilon_{QD} + 2\varepsilon)$

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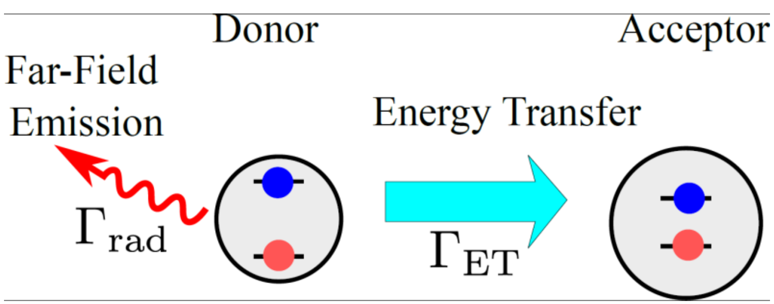


$$\frac{1}{\tau_D} = \Gamma_{rad,0} + \Gamma_D$$

$$\Gamma_D = \Gamma_{ET} + \Delta\Gamma_{rad}$$

Non radiative life time: $\tau_A = 1/(2\gamma_A)$

$\mathbf{d}_D \quad E_D = \hbar\omega_D \qquad \mathbf{d}_A \quad E_A = \hbar\omega_A$

Donor decay:

$$\boxed{\Gamma_{\rm D} = \frac{2}{\hbar}\,\mathrm{Im}\left[\frac{1}{\omega_{\rm A} - \mathrm{i}\gamma_{\rm A} - \omega_{\rm D}}\frac{1}{\hbar^2}\left(\boldsymbol{d}_{\rm D}\cdot\hat{G}(\boldsymbol{r})\boldsymbol{d}_{\rm A}\right)^2\right]}$$

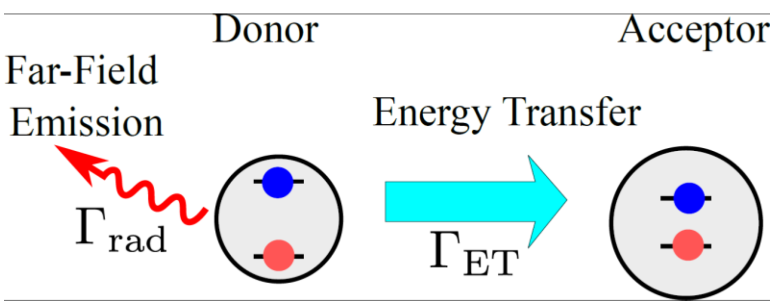
Small separation (long wavelength limit):

$$qr \ll 1 \quad \Rightarrow \quad \Gamma_{D,0} = \frac{2\pi}{\hbar}\frac{1}{\pi\hbar}\frac{\gamma_{\rm A}}{(\omega_{\rm D} - \omega_{\rm A})^2 + \gamma_{\rm A}^2}|\boldsymbol{d}_{\rm D}\hat{G}_0\boldsymbol{d}_{\rm A}|^2 = \Gamma_{\rm ET,0}$$

Large separation:

$$\boxed{\Delta\Gamma_{rad} = \Gamma_D - \Gamma_{ET}}$$

[1] A. N. Poddubny, A. V. Rodina, Nonradiative and radiative Förster energy transfer between quantum dots, JETP. **122**, 531 (2016).



$$\mathbf{d}_D \quad E_D = \hbar\omega_D \qquad \mathbf{d}_A \quad E_A = \hbar\omega_A$$

$$\frac{1}{\tau_D} = \Gamma_{rad,0} + \Gamma_D$$

$$\Gamma_D = \Gamma_{ET} + \Delta\Gamma_{rad}$$

Non radiative life time: $\tau_A = 1/(2\gamma_A)$

$$\boxed{\Gamma_{\rm D} = \frac{2}{\hbar}\,\mathrm{Im}\left[\frac{1}{\omega_{\rm A} - \mathrm{i}\gamma_{\rm A} - \omega_{\rm D}}\frac{1}{\hbar^2}\left(\boldsymbol{d}_{\rm D}\cdot\hat{G}(\boldsymbol{r})\boldsymbol{d}_{\rm A}\right)^2\right]}$$

$$\boxed{\Gamma_{\rm ET} = \frac{2\pi}{\hbar}\Theta|\boldsymbol{d}_{\rm D}\cdot\hat{G}\boldsymbol{d}_{\rm A}|^2}$$

$$\boxed{g = \boldsymbol{d}_{\rm D}\hat{G}\boldsymbol{d}_{\rm A}}$$

$$\boldsymbol{d}_A \parallel \boldsymbol{d}_D \parallel \boldsymbol{r}$$

$$g_{\parallel} = d_A d_D \frac{e^{iqr}}{\varepsilon}\left(\frac{2}{r^3} - \frac{2iq}{r^2}\right)$$

$$\boldsymbol{d}_A \parallel \boldsymbol{d}_D \perp \boldsymbol{r}$$

$$g_{\perp} = d_A d_D \frac{e^{iqr}}{\varepsilon}\left(-\frac{1}{r^3} + \frac{iq}{r^2} + \frac{q^2}{r}\right)$$

Numerical results:

$$\tau_A = 1\ \text{ps},\ E_\mathrm{D} = \hbar\omega_\mathrm{D} = 2\ \text{eV}$$

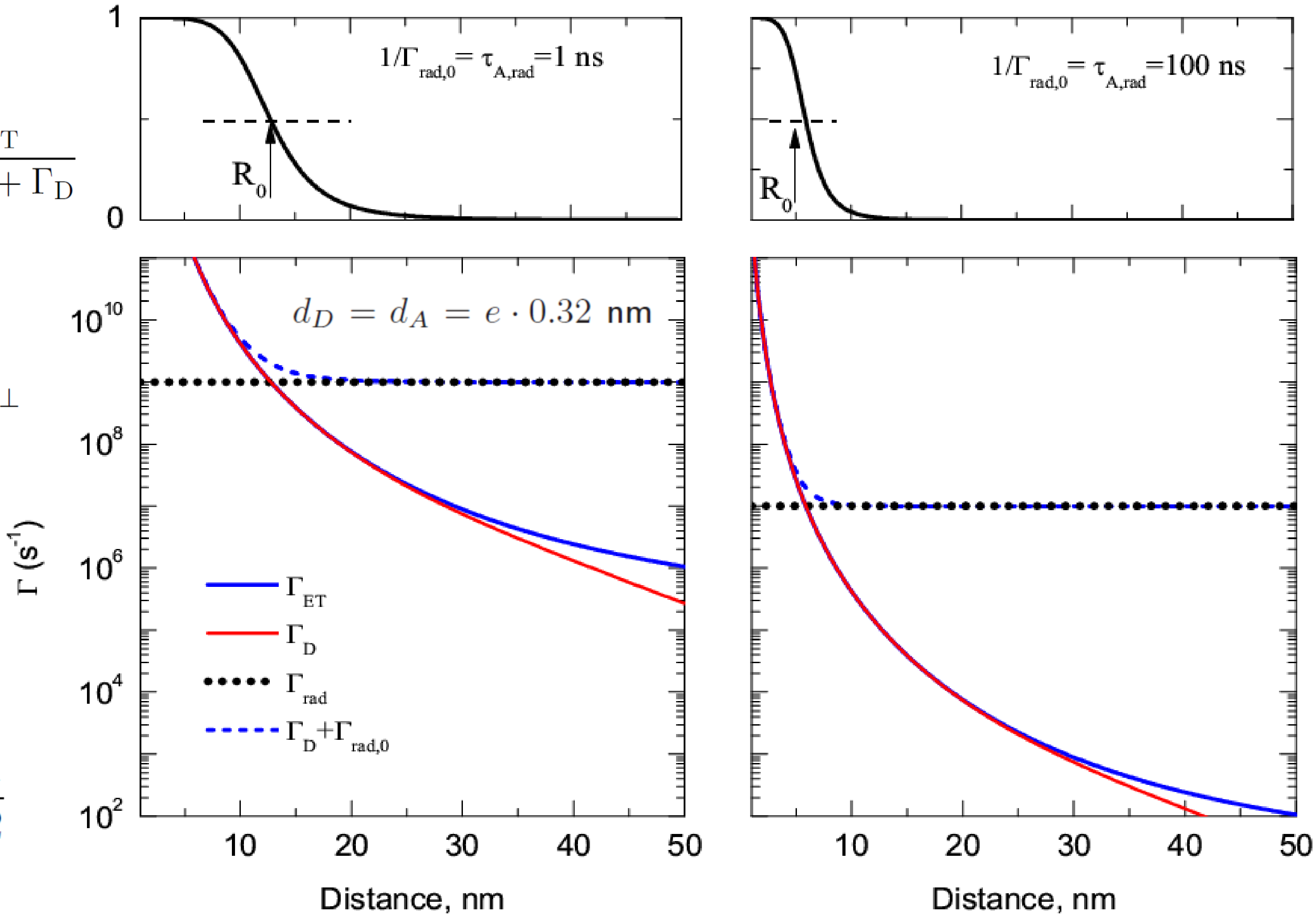
$$\Delta = \omega_\mathrm{D} - \omega_\mathrm{A} = 0$$

$$K_\mathrm{ET} = \frac{\Gamma_\mathrm{ET}}{\Gamma_{\mathrm{rad},0} + \Gamma_\mathrm{D}}$$

$$\Gamma = \frac{1}{3}\Gamma_\parallel + \frac{2}{3}\Gamma_\perp$$

Förster radius:

$$K_\mathrm{ET}(R_0) = \frac{1}{2}$$



Effective ET at *r* <2 *R*$_0$ is the non radiative process and determines the modification of the donor life time

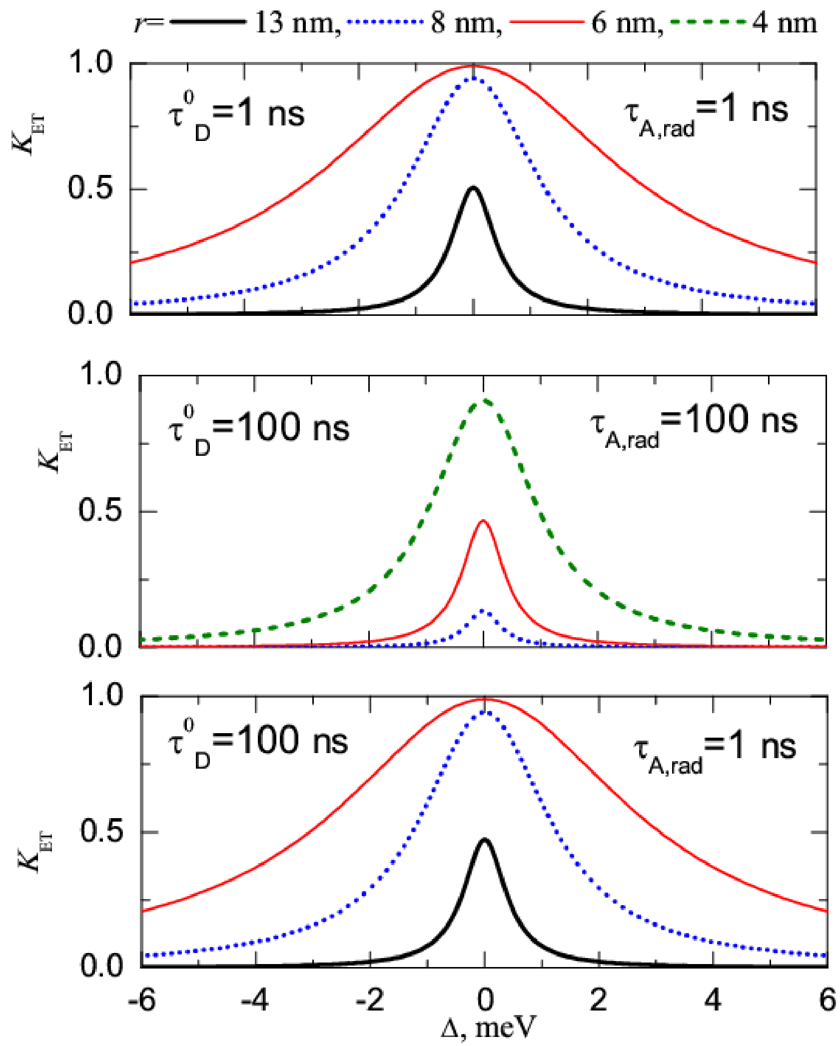
Numerical results:

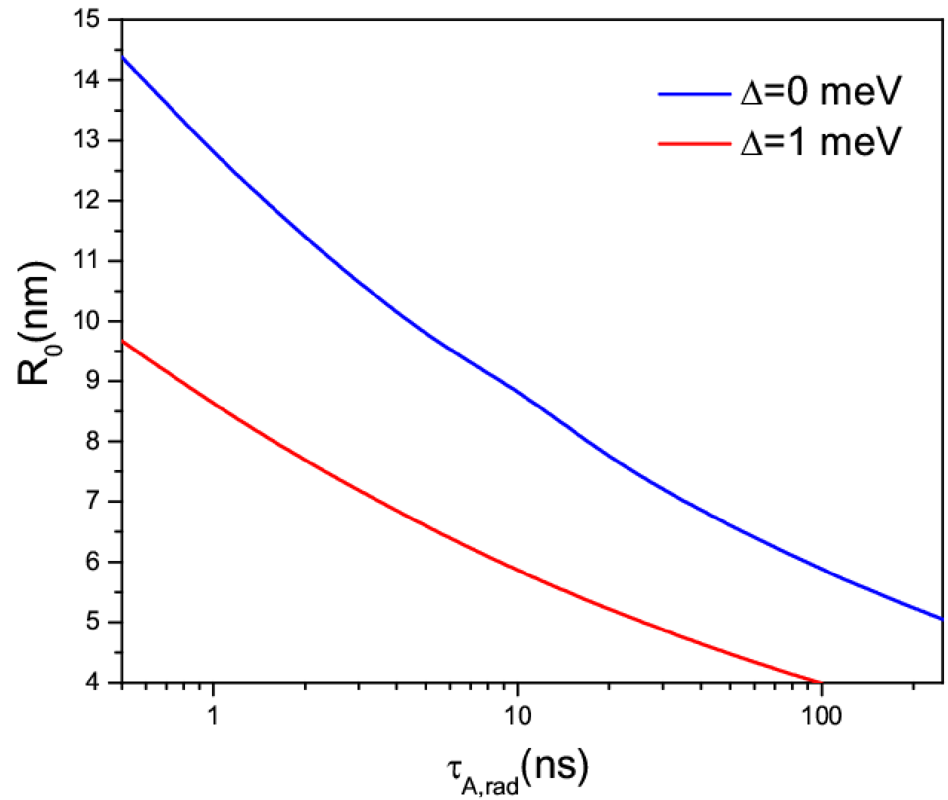
$$\tau_A = 1 \text{ ps}, \; E_D = \hbar\omega_D = 2 \text{ eV}$$

FRET efficiency: $$K_{ET} = \frac{\Gamma_{ET}}{\Gamma_{rad,0} + \Gamma_{ET}}$$

Förster radius: $$K_{ET}(R_0) = \frac{1}{2}$$

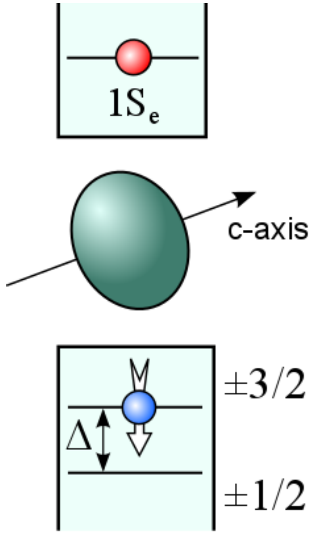
$$\Gamma_{ET} = \Gamma_{rad,0}\left(\frac{R_0}{r}\right)^6$$





Förster radius depends strongly on the acceptor radiative rate

Band edge exciton fine structure:



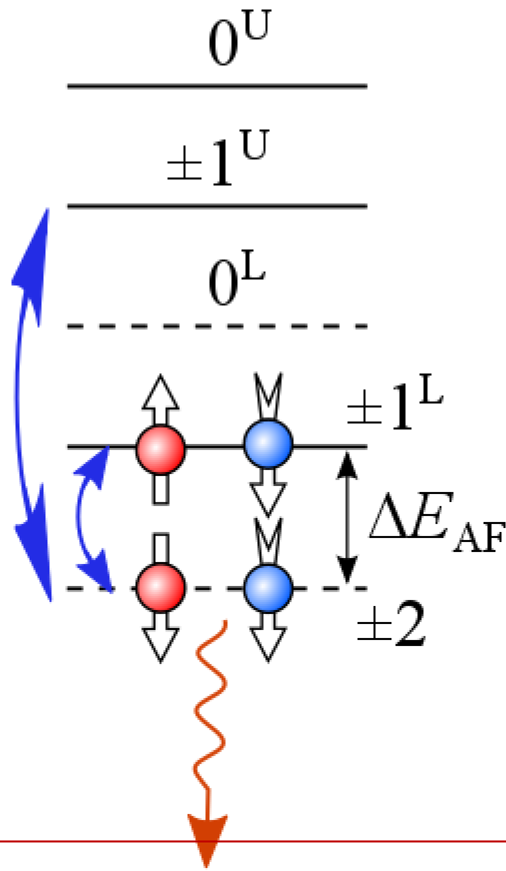
Effect of the
non spherical shape

CdSe NC

electron-hole
exchange
interaction

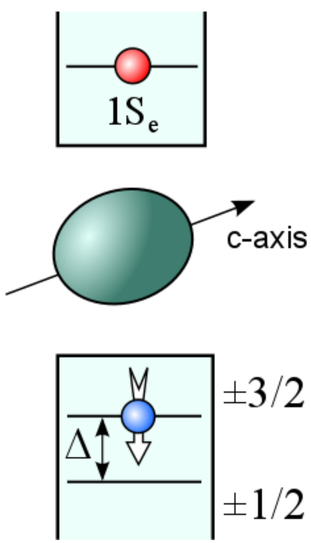
$$\eta \propto \left(\frac{a_{exc}}{a}\right)^3$$

Al. Efros, et al.,
PRB (1996)



"A"-
bright (active) exciton

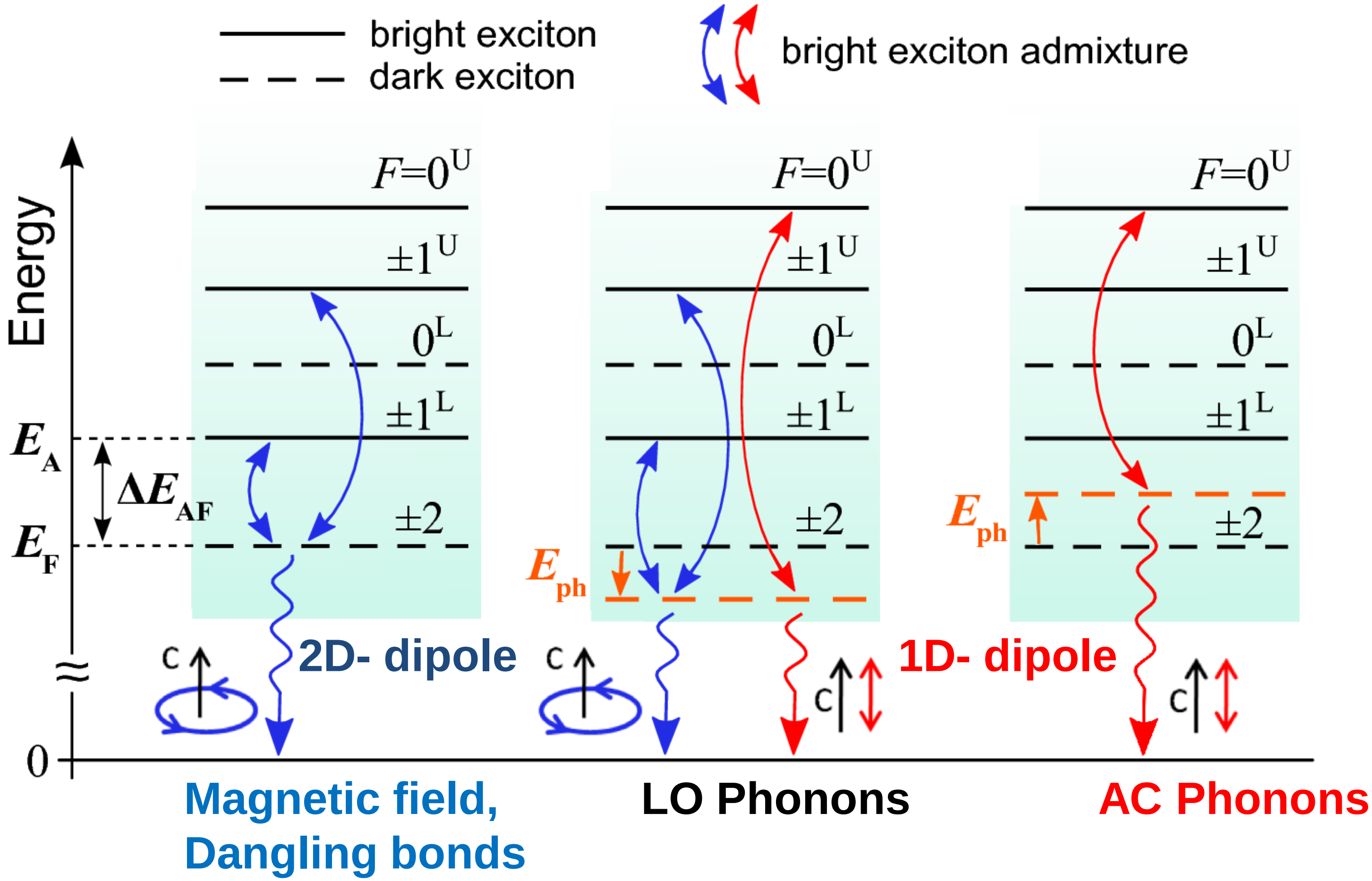
"F"-
dark (forbidden) exciton –
Occupied at T=4.2 K



CdTe NC

Dark exciton radiative recombination

Activation of the dark exciton recombination



A.Rodina and Al.L. Efros, Nano Letters 2015, 15, 4214

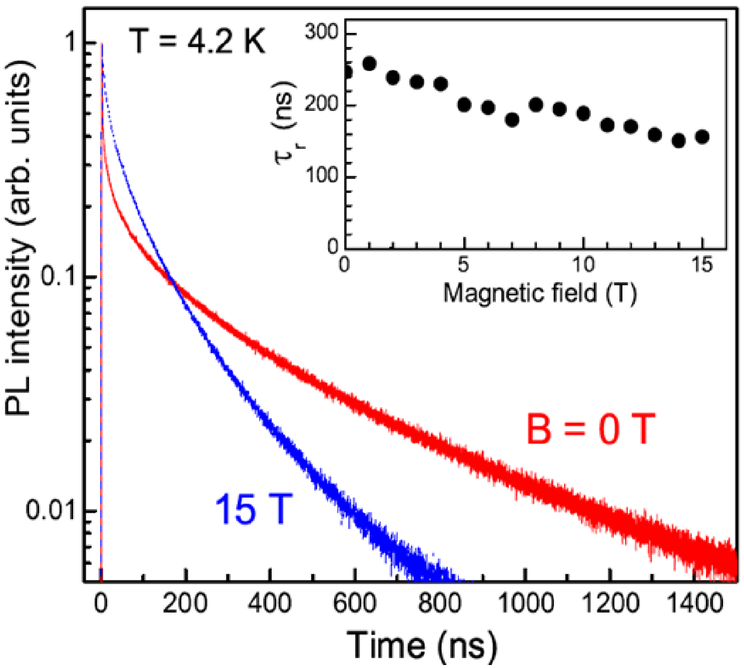
A.Rodina and Al.L. Efros, Phys. Rev. B 93, 155427 (2016)

L.Biadala et al., Nature Nanotechnology,doi:10.1038/nnano.2017.22, (2017)

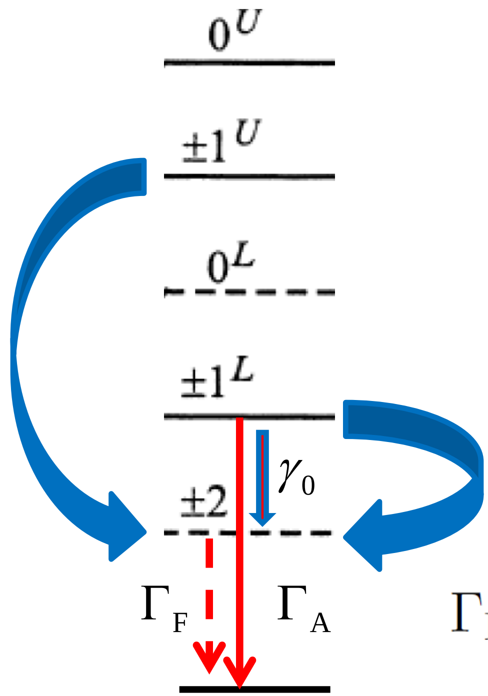
Dark exciton is activated by admixture of the bright exciton states

Activation of the dark exciton PL in magnetic field

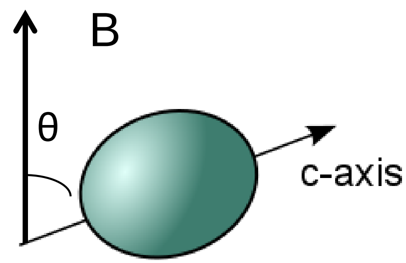
CdTe NC (d=3.4 nm)



F. Liu, A. V. Rodina, D. R. Yakovlev et al.
Phys. Rev. B (2014)



Al. Efros, et al., PRB (1996)



$$\Gamma_{\mathrm{F}} \propto |d_{\mathrm{F}}|^2 = |d_{\mathrm{F}}^0|^2 + |d_{\mathrm{F}}^B|^2$$

$$|d_{\mathrm{F}}^B|^2 \propto B^2$$

Dark exciton has dipole momentum and participates in PL.
Can dark exciton participate in FRET ?

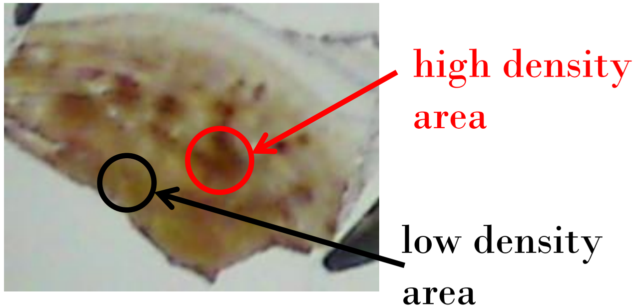
Magnetic field enhancement of Förster energy transfer in ensemble of colloidal CdTe nanocrystals

[2] Phys. Rev. B **92**, 125403 (2015)

Feng Liu,[1,2] A. V. Rodina,[3] D. R. Yakovlev,[1,3] A. A. Golovatenko,[3] A. Greilich,[1] E. D. Vakhtin,[4] A. Susha,[5] A. L. Rogach,[5] Yu. G. Kusrayev[3] and M. Bayer[1,3]

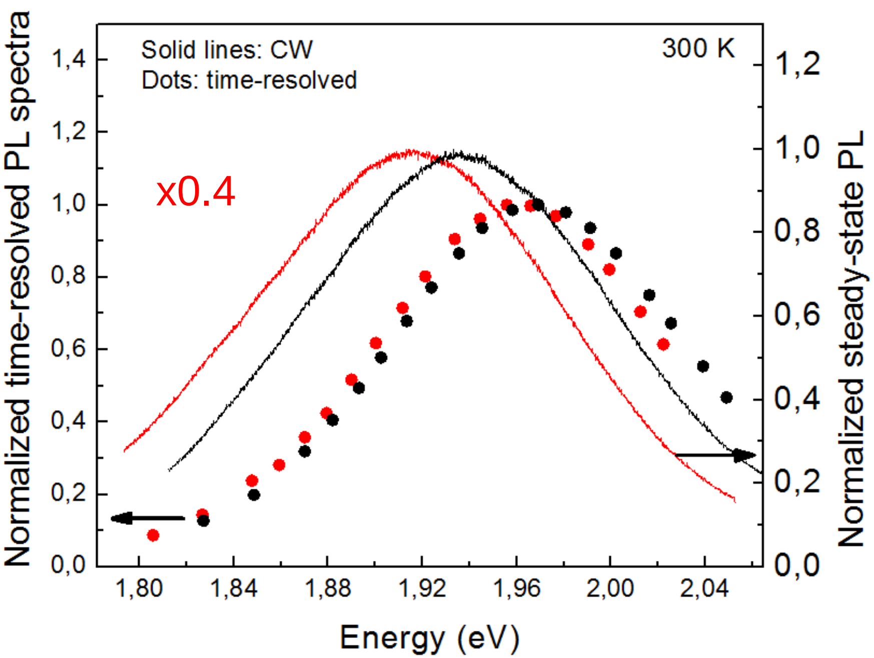
[1] *Experimentelle Physik 2, Technische Universität Dortmund, 44221 Dortmund, Germany*
[2] *University of Sheffield, Sheffield, S3 7RH, United Kingdom*
[3] *Ioffe Institute, Russian Academy of Sciences, 194021 St. Petersburg, Russia*
[4] *St. Petersburg State Polytechnical University, 195251 St. Petersburg, Russia and*
[5] *City University of Hong Kong, Hong Kong*

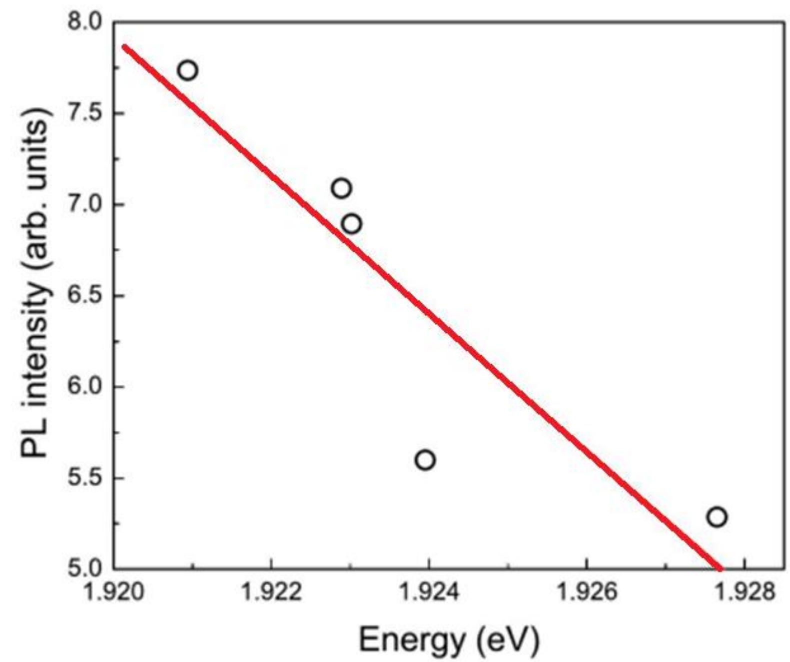
Experiment: CdTe nanocrystals (d=3.4 nm)
Shift of PL maximum in CW



High density area
- large shift (49 meV)
- High energy transfer efficiency

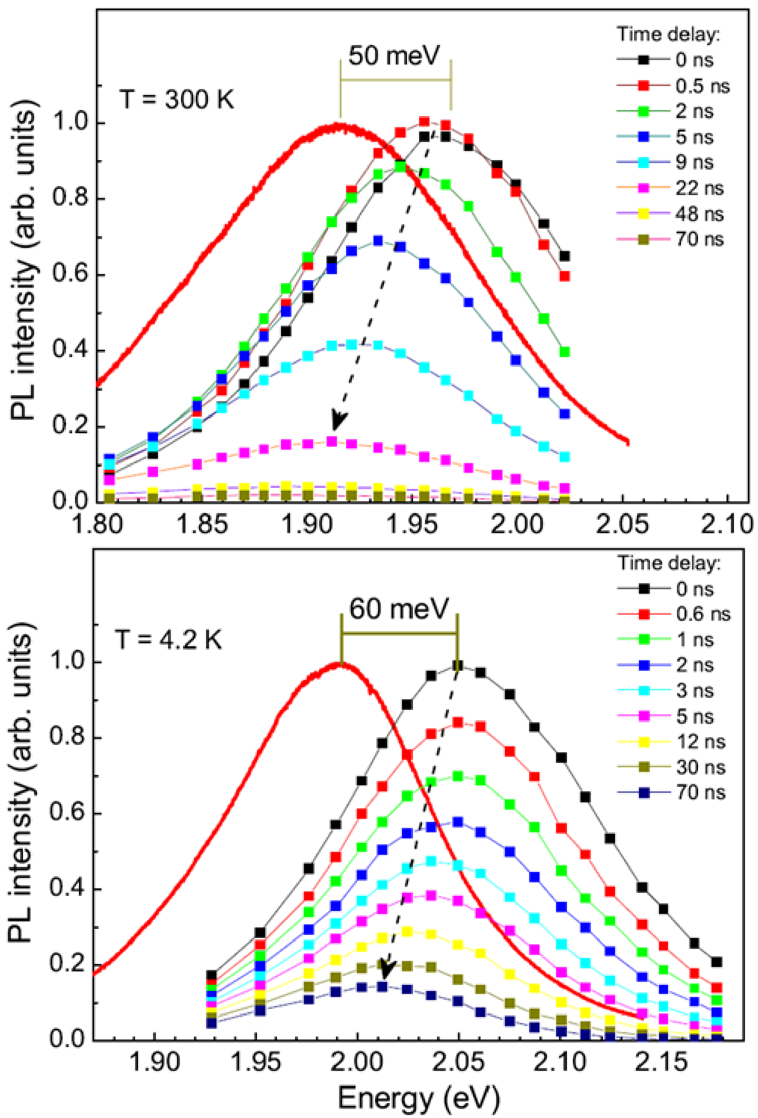
Low density area
- small shift (30 meV)
- low energy transfer efficiency

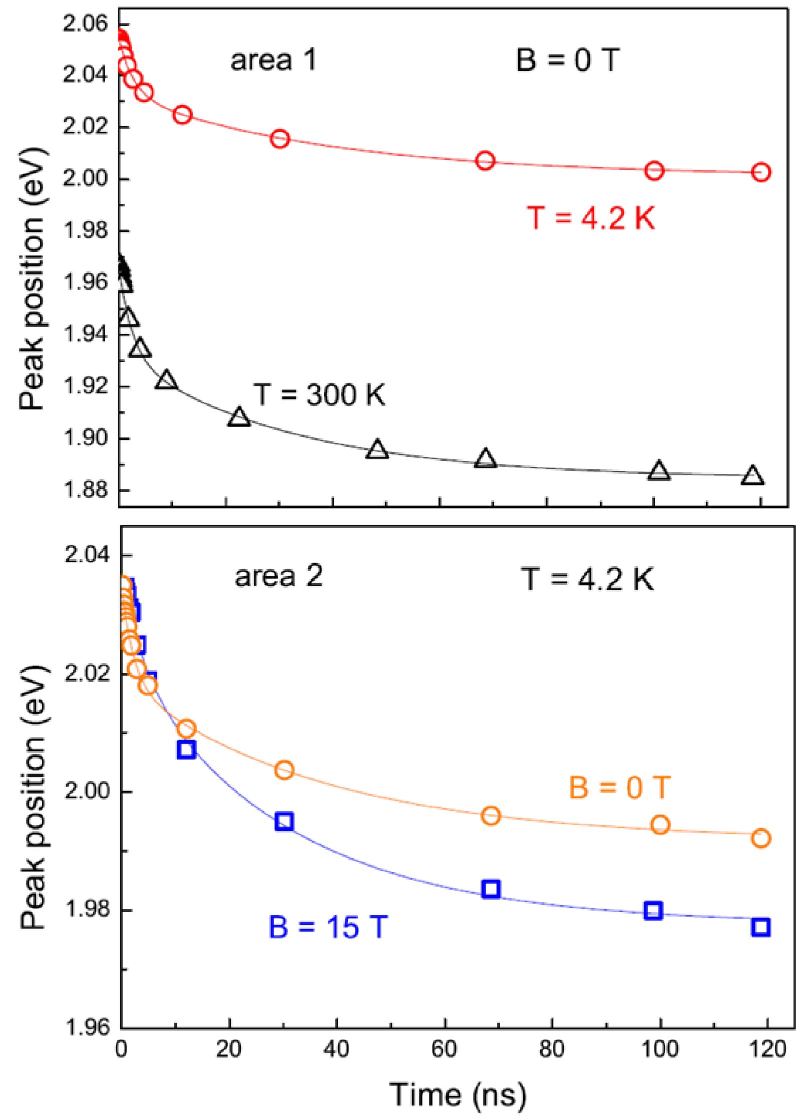




Shift of PL maximum ~ Density of NCs (distance between NCs) !

CW and Time-resolved shift of the PL maximum

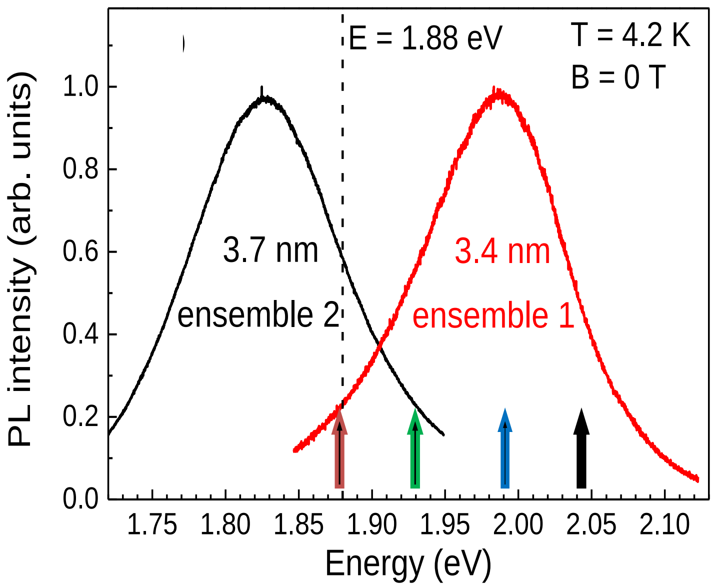


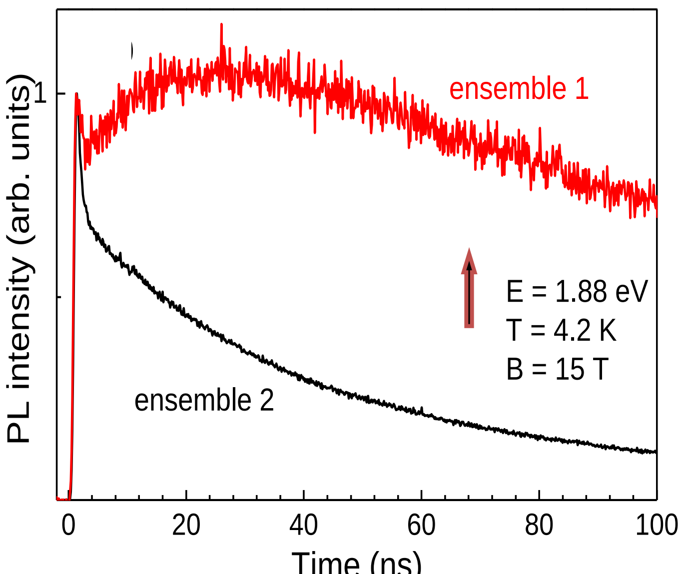


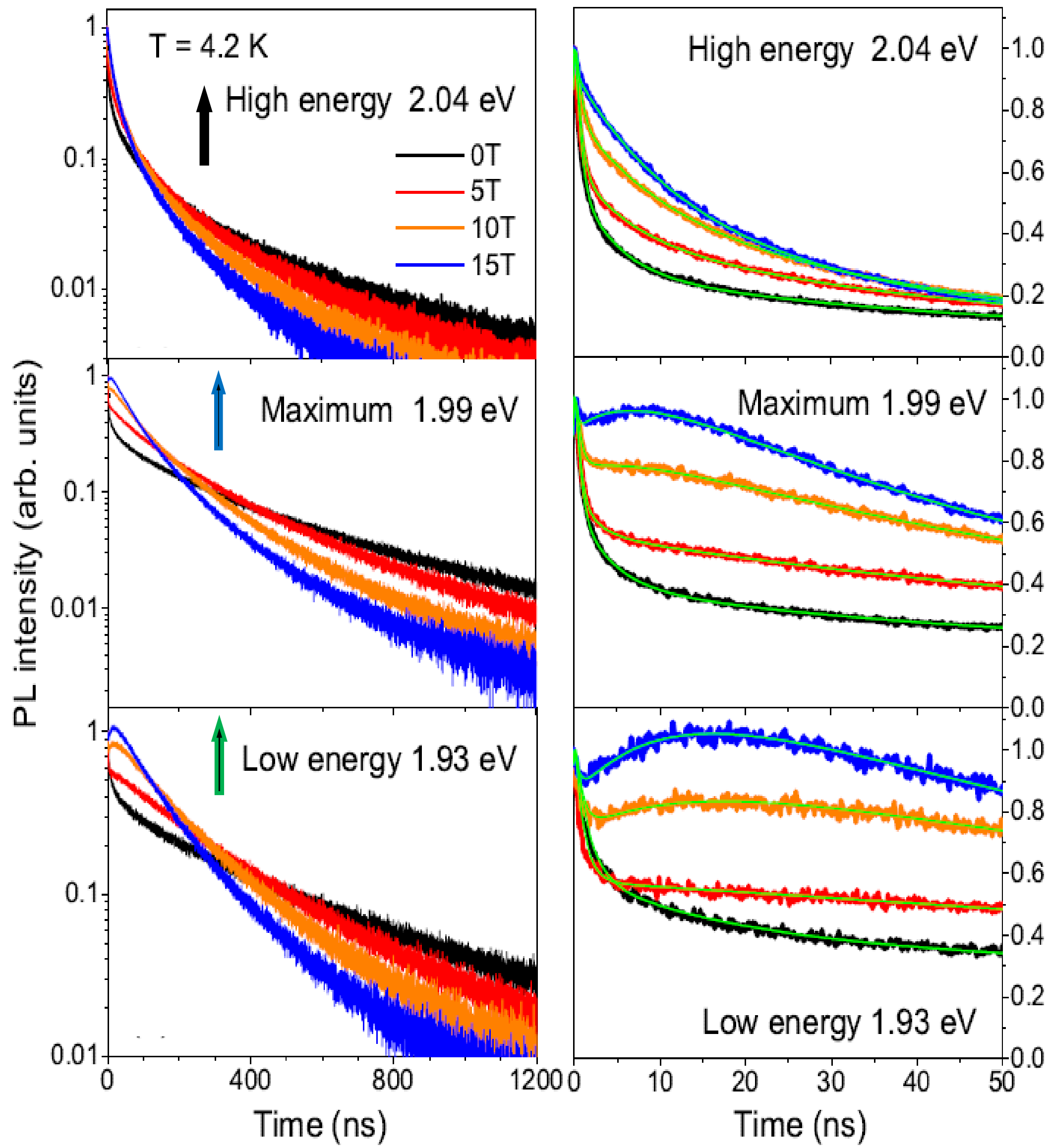
CW PL shift does not depend on B

Time-resolved PL shift depends on B !

Spectral dependence of the PL dynamics

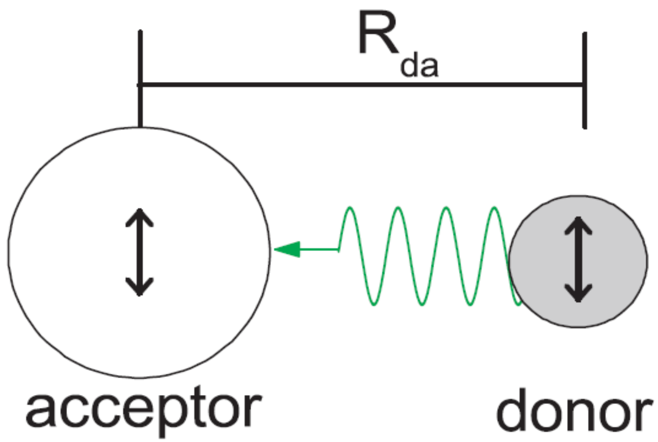


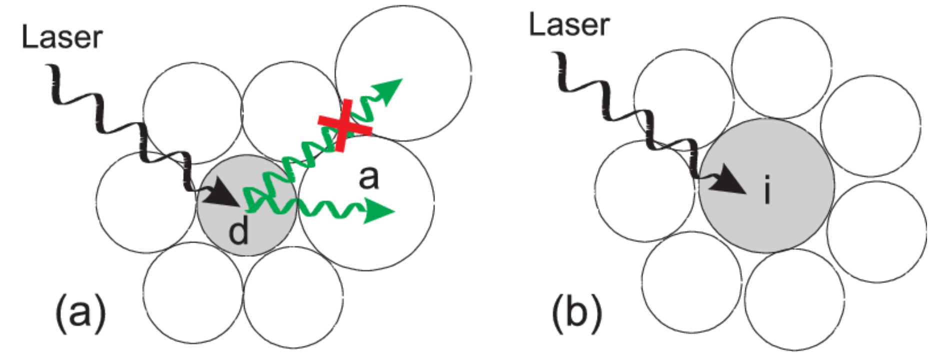


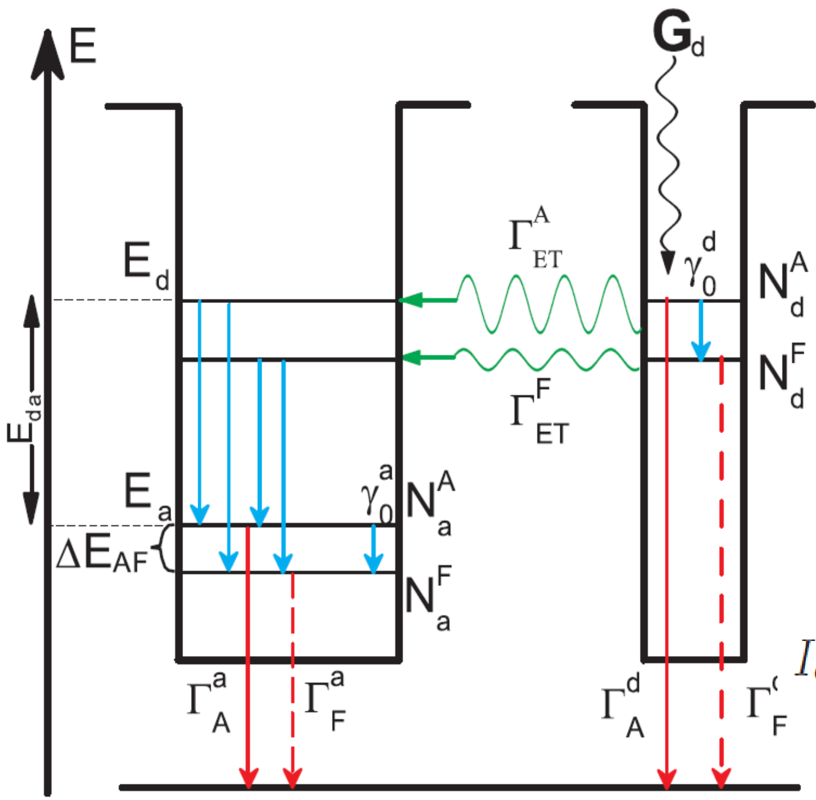


PL decay depends on the energy. The difference is due to the ET !

Model of the energy transfer







Exciton populations

$$N(E,t) = N_{\mathrm{i}}(E,t) + N_{\mathrm{d}}(E,t) + N_{\mathrm{a}}(E,t)$$

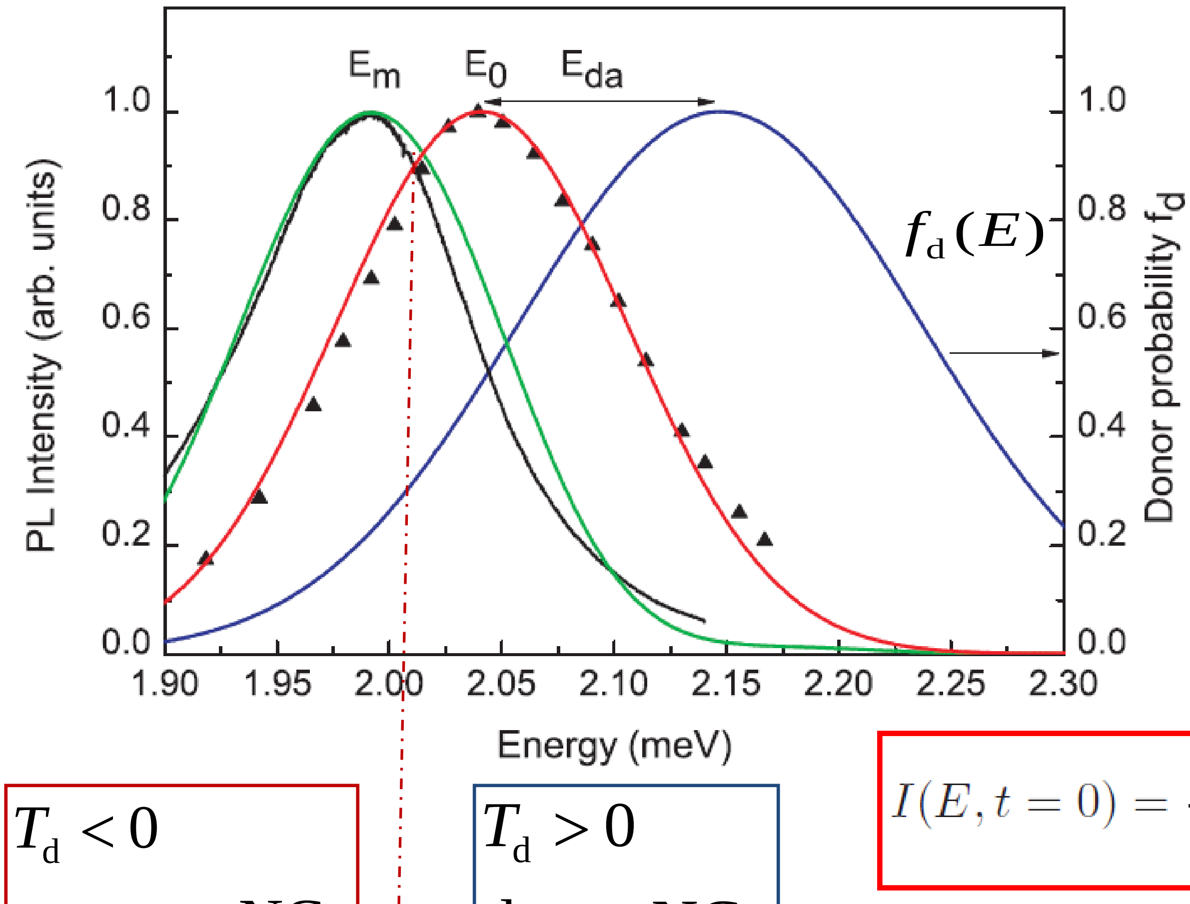
$$N_{\mathrm{d,i,a}}(E,t) = N^{\mathrm{A}}_{\mathrm{d,i,a}}(E,t) + N^{\mathrm{F}}_{\mathrm{d,i,a}}(E,t)$$

$$I(E,t) = I_{\mathrm{i}}(E,t) + I_{\mathrm{d}}(E,t) + I_{\mathrm{a}}(E,t)$$

$$I_{\mathrm{d,i,a}}(E,t) = \Gamma^{\mathrm{rad}}_{\mathrm{A}}(E) N^{\mathrm{A}}_{\mathrm{d,i,a}}(E,t) + \Gamma^{\mathrm{rad}}_{\mathrm{F}}(E) N^{\mathrm{F}}_{\mathrm{d,i,a}}(E,t)$$

PL dynamics

Shift of the PL spectrum in CW regime



E_{da} = 105 meV

$$N_d^0(E) = N_0(E)\, f_{\mathrm{d}}(E)$$

$$I(E, t=0) = \frac{I}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(E-E_0)^2}{2\sigma^2}\right]$$

$T_{\mathrm{d}} < 0$

acceptor NCs

$T_{\mathrm{d}} > 0$

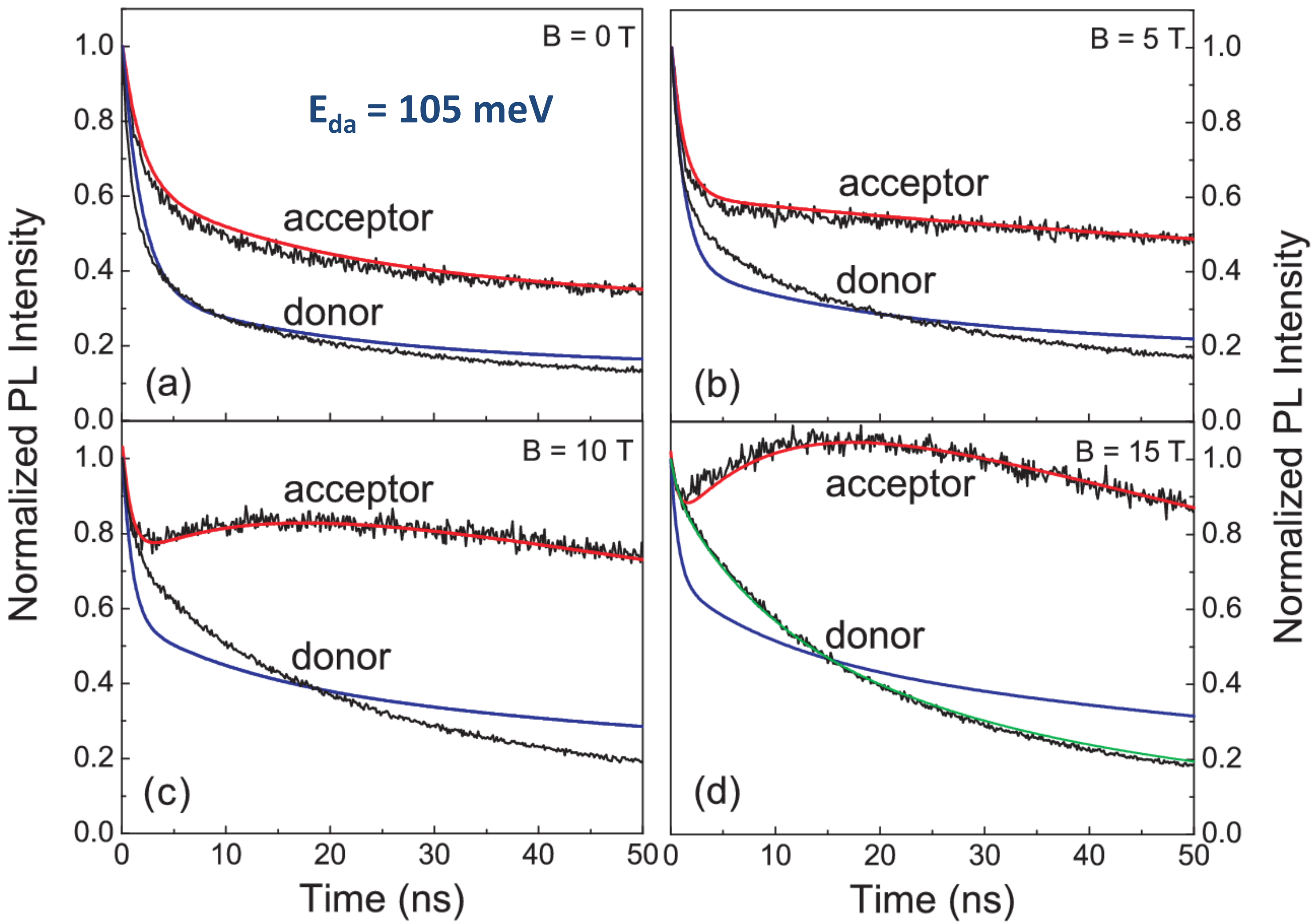
donor NCs

$$I_{\mathrm{PL}}^{\mathrm{CW}}(E) = I(E, t=0)\left[1 - K_{\mathrm{ET}} T_{\mathrm{d}}(E)\right],$$

$$T_{\mathrm{d}}(E) = f_{\mathrm{d}}(E) - f_{\mathrm{d}}(E + E_{\mathrm{da}}) \frac{N_0(E+E_{\mathrm{da}})}{N_0(E)}$$

$$K_{\mathrm{ET}} = \frac{\Gamma_{\mathrm{ET}}^{\mathrm{F}}}{\Gamma_{\mathrm{ET}}^{\mathrm{F}} + \Gamma_{\mathrm{F}}}$$

Effect of the magnetic field on the PL dynamics: Simulations with ET



Effect of the magnetic field on

dark exciton recombination rate:

$$\Gamma_F(B)/\Gamma_F(0) = 1 + (B/12)^2$$

energy transfer rate:

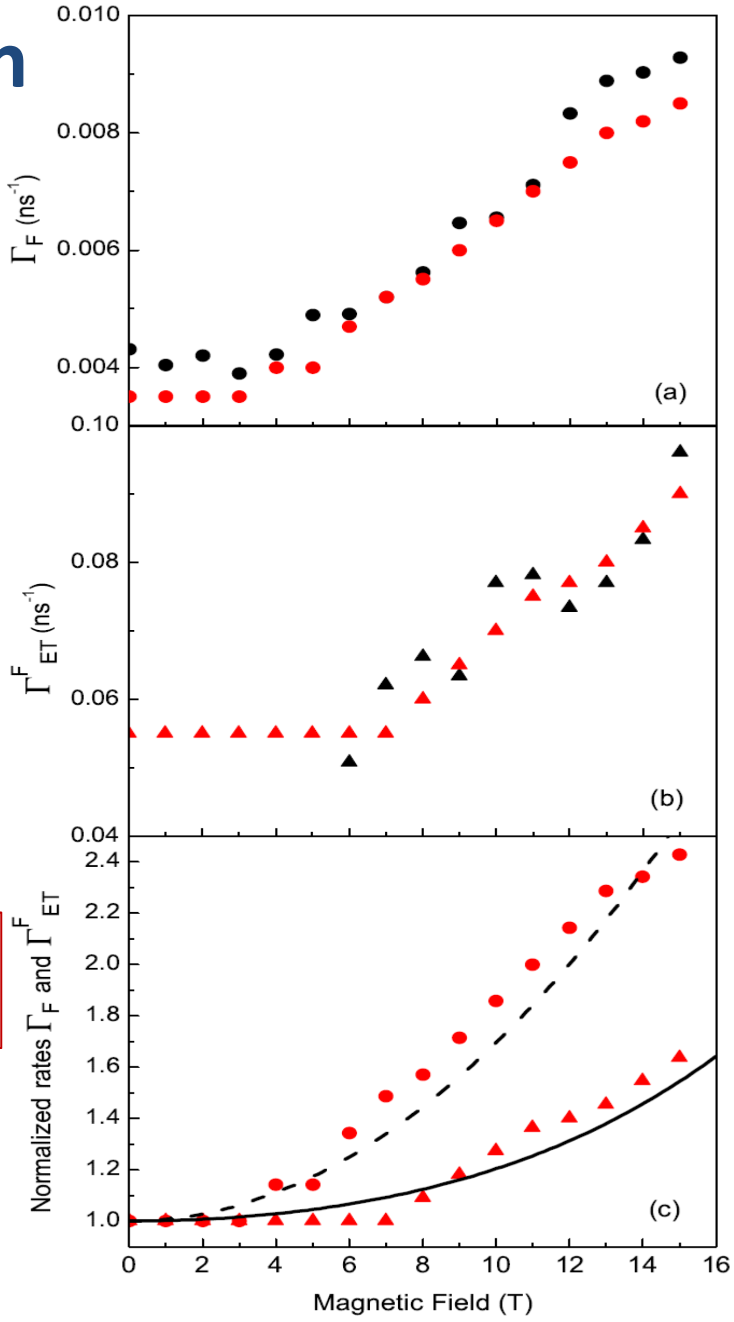
$$\Gamma_{ET}^F(B)/\Gamma_{ET}^F(0) = 1 + (B/12)^2 + (B/24)^4$$

Dark exciton in donor NC:

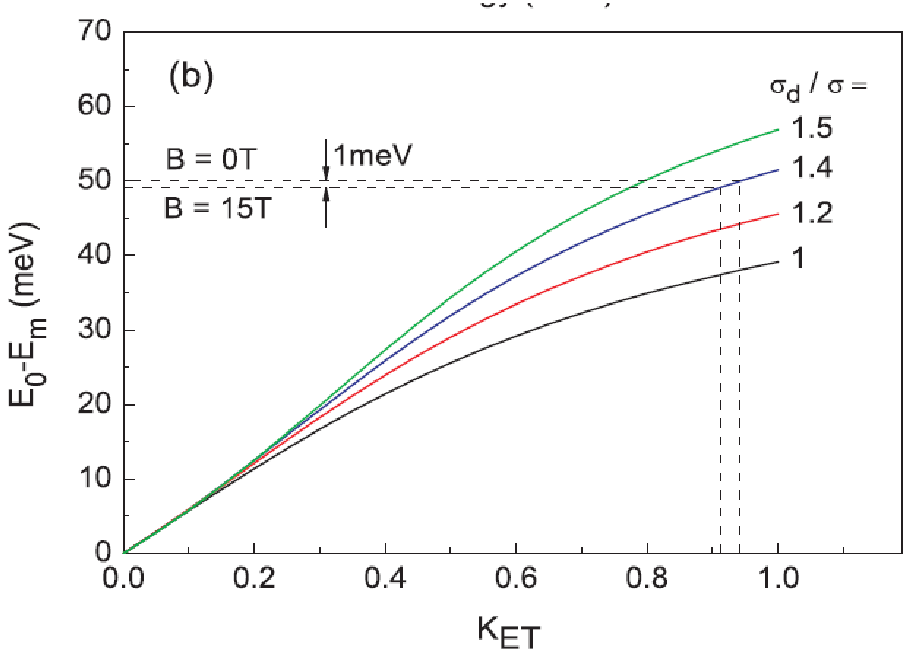
Dark exciton in donor and acceptor NCs:

energy transfer efficiency:

$$K_{ET}(B) = \frac{\Gamma_{ET}^F}{\Gamma_{ET}^F + \Gamma_F} \approx \text{Const}$$



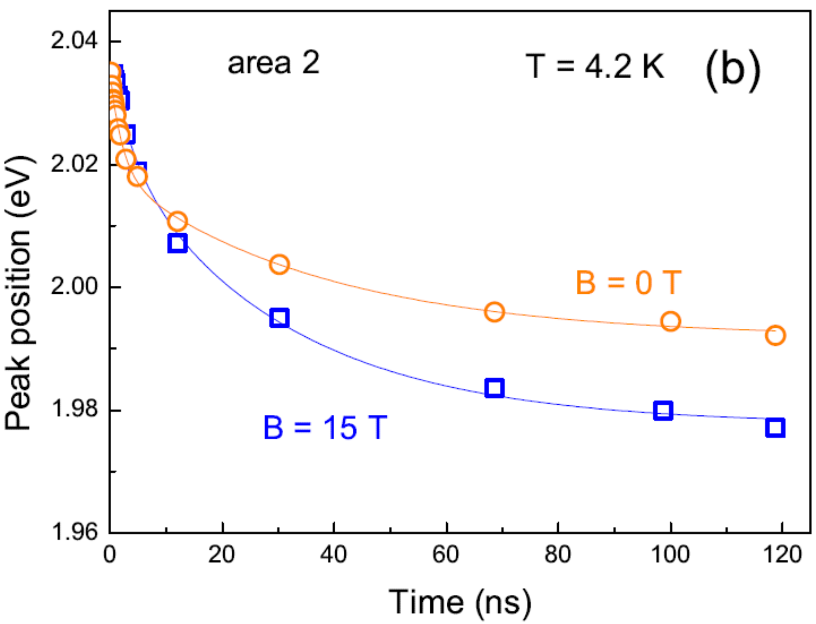
Effect of the magnetic field on the PL shift



K_{ET} does not depend on B

$$E_0 - E_m(\mathrm{CW}) = \Delta[E_m]K_{ET}$$

CW PL shift does not depend on B

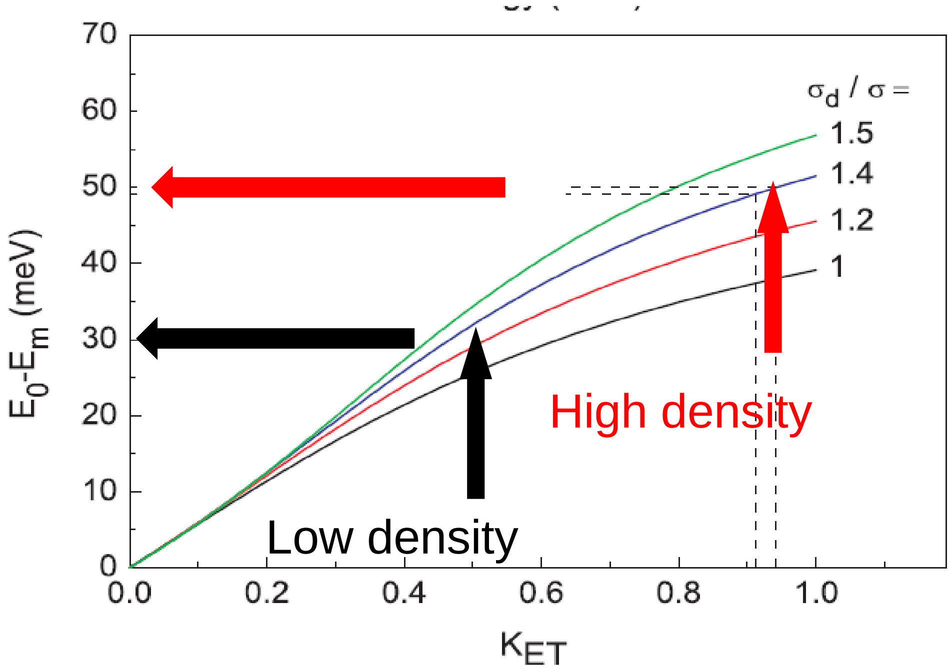


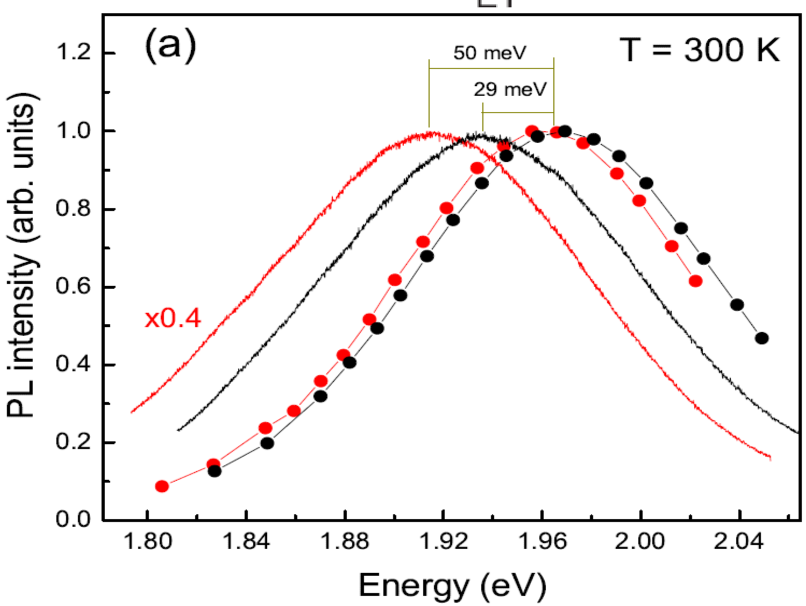
Γ_{ET}^{F} is increased in B

$$E_0 - E_m(t) = \Delta[E_m(t)][1 - \mathrm{Exp}(-\Gamma_{ET}^{F} t)]$$

Time-resolved PL shift is increased in B

Effect of the NC density on the CW PL shift:





ET Förster radius

$$K_{\mathrm{ET}} \approx 0.5 \Rightarrow R_{\mathrm{da}} \approx R_0$$

Comparison of two areas:

$$R_{\mathrm{da}} / R_{\mathrm{da}} \approx 3/2$$

$$I_{\mathrm{Low}} / I_{\mathrm{High}} \approx 4/9$$

$$R_{\mathrm{da}} \approx d$$

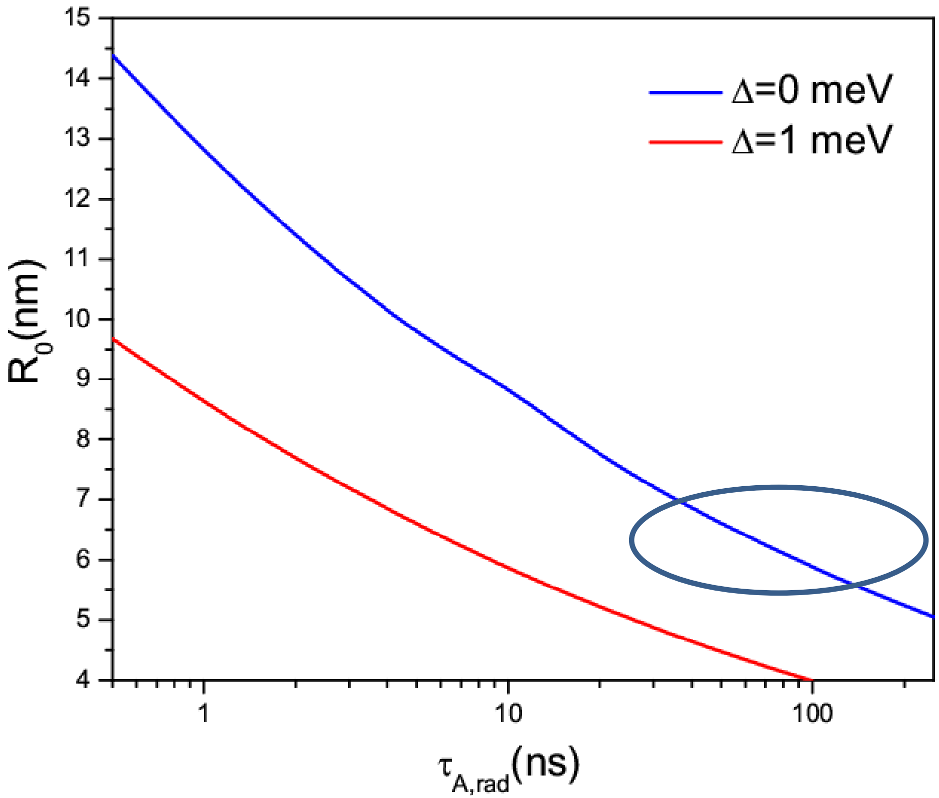
$R_0 \approx 5 \div 6$ nm -

Förster radius

ET Förster radius in ensemble of CdTe colloidal NCs :

Numerical results:

$$\tau_A = 1 \text{ ps}, \; E_{\mathrm{D}} = \hbar\omega_{\mathrm{D}} = 2 \text{ eV}$$



Experimental results at 4.2 K:

$$\Gamma^{\mathrm{F}}_{\mathrm{ET}}(R_{\mathrm{da}}) = \Gamma_{\mathrm{F}} \left(\frac{R_0}{R_{\mathrm{da}}} \right)^6$$

$R_0 \approx 5 \div 6$ nm -

Förster radius

At low temperatures ET in ensemble of CdTe colloidal NCs is dominated by the FRET from dark exciton states

Förster Resonance Energy Transfer in arrays of CdSe/ZnSe quantum dots

[3] A.A. Golovatenko, M.A. Semina, A.V. Rodina, T.V. Shubina. Density of states and photoluminescence spectra in the dense arrays of CdSe/ZnSe quantum dots with Gaussian potential profile. – Acta Physica Polonica A **129**, 107 (2016).

[4] Shubina,TV; Rodina,AV; Semina,MA; Golovatenko,AA; Toropov,AA; Rakhlin,MV; Sedova,IV; Sorokin,SV; Gronin,SV; Sitnikova,AA; Kuritsyn,DI; Sergeev,SM; Krasil`nik,ZF; Ivanov,SV. Spectral selection of excitonic transitions in a dense array of CdSe/ZnSe quantum dots. Phys. Status Solidi B 253, 1485 (2016).

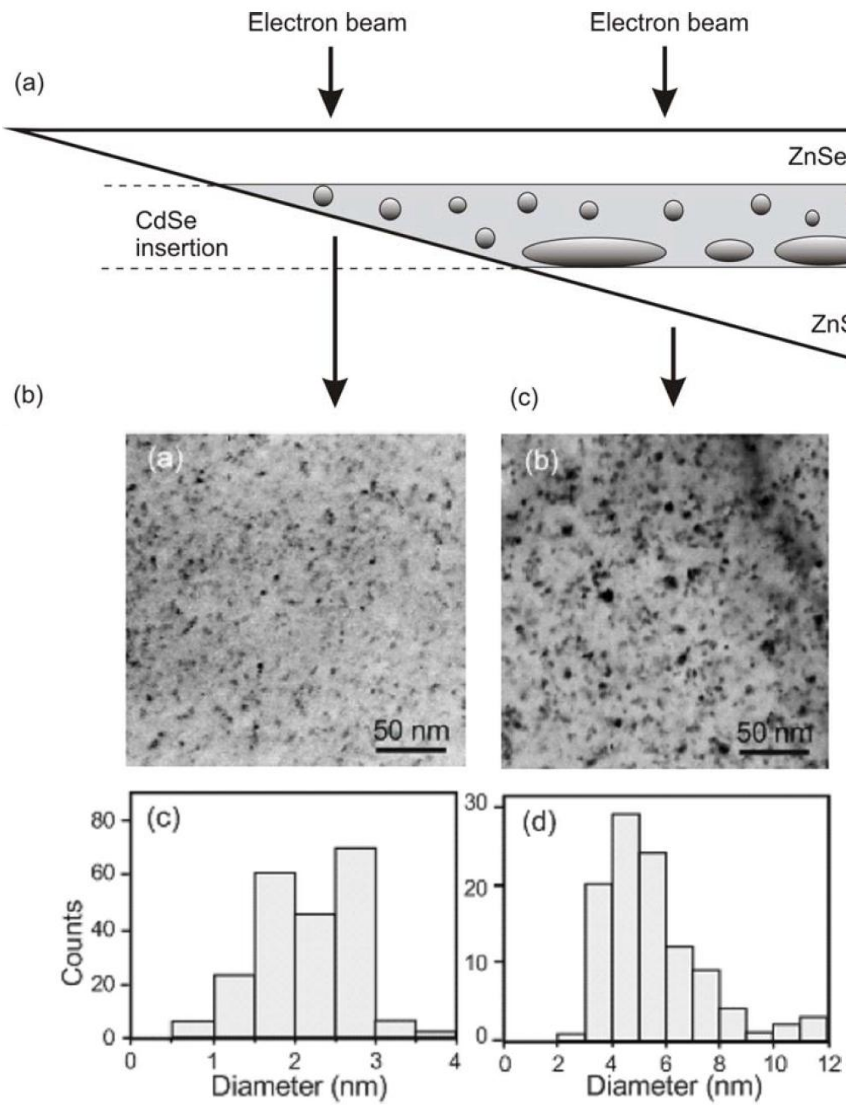
[5] TV Shubina, MA Semina, KG Belyaev, AV Rodina, AA Toropov, SV Ivanov, Förster Resonance Energy Transfer and Harvesting in II–VI Fractional Monolayer Structures, Journal of Electronic Materials, 1-5 (2016).

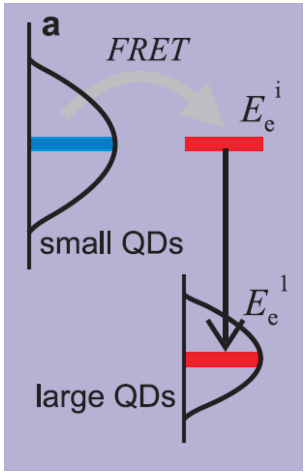
[6] TV Shubina, KG Belyaev, MA Semina, AV Rodina, AA Golovatenko, AA Toropov, SV Sorokin, IV Sedova, V Yu Davydov, AN Smirnov, PS Kop’ev, SV Ivanov. Resonance energy transfer in a dense array of II–VI quantum dots. Physics of the Solid State 58, 2256-2260 (2016).

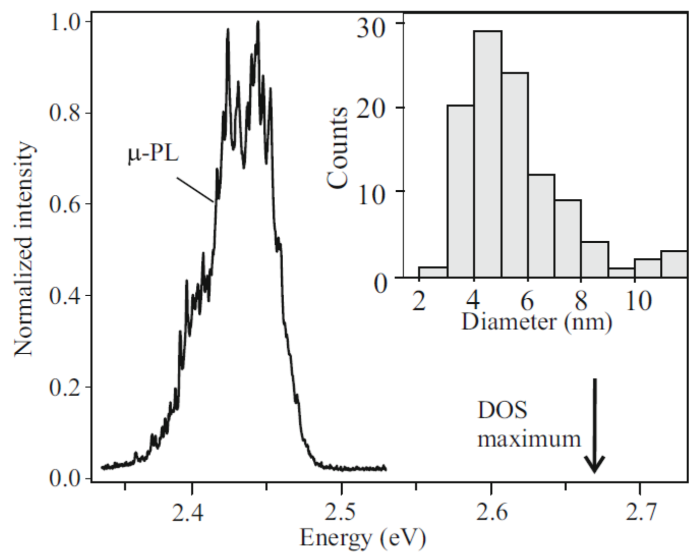
Ioffe Institute, St. Petersburg, Russia

FRET in single dense array of CdSe/ZnSe quantum dots

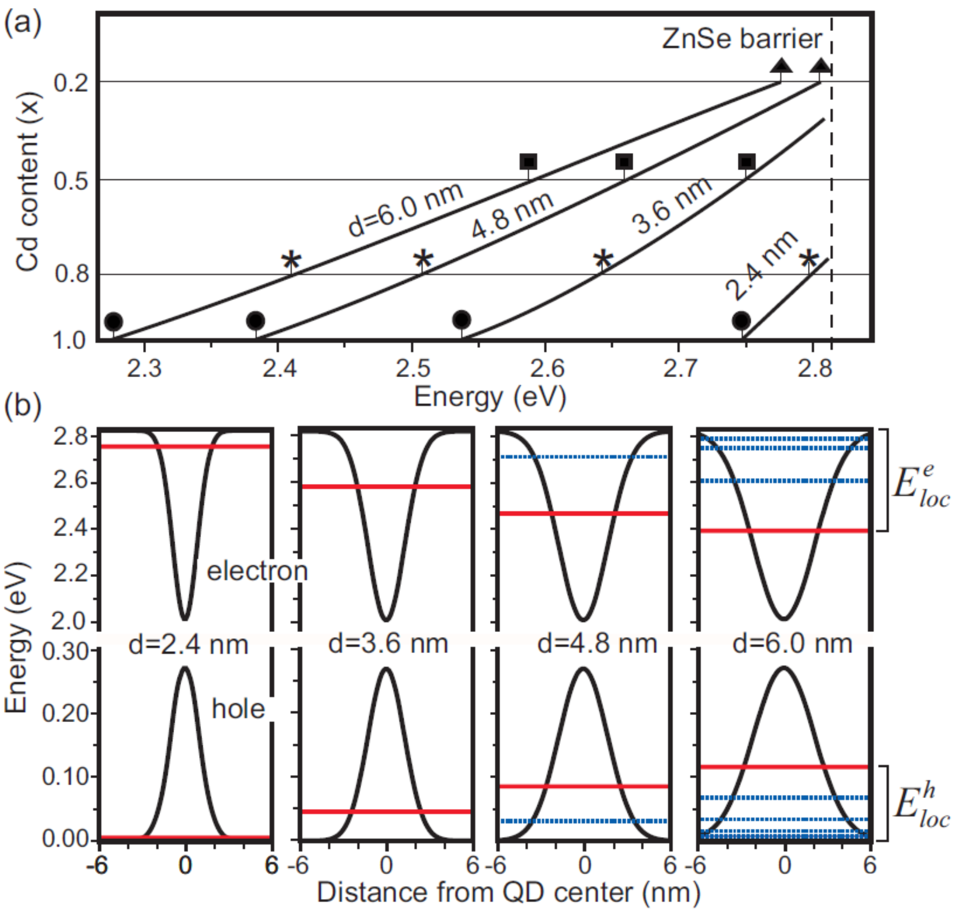
MBE

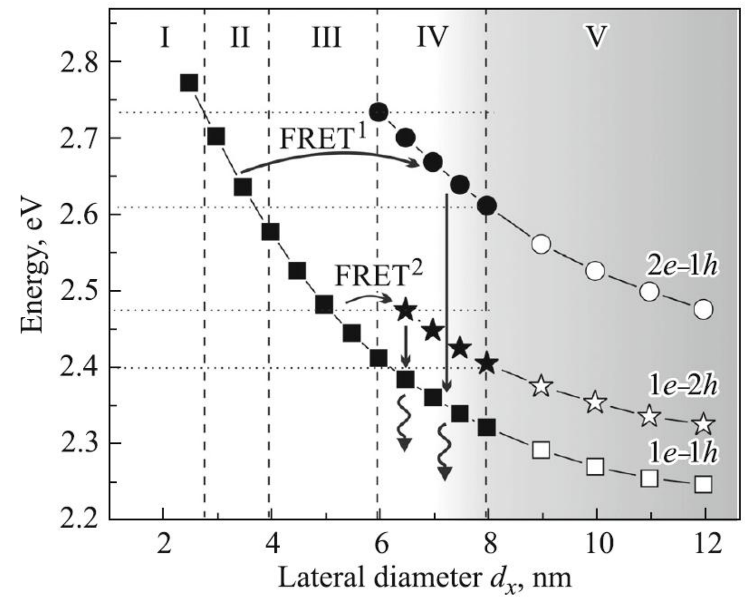






FRET in single dense array of CdSe/ZnSe quantum dots

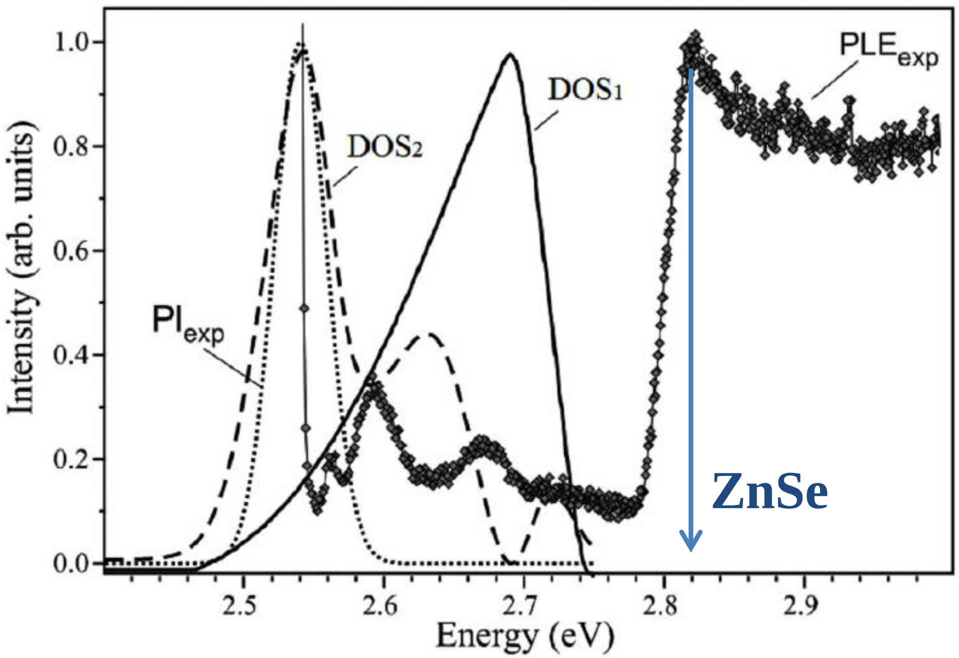


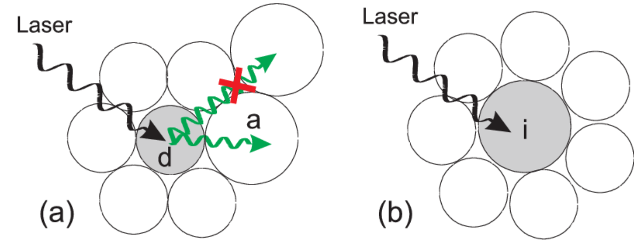


$$V^{e,h}_{\text{sph}} = V^{e,h}_{\text{off}} \left(1 - \exp\left[-\frac{4r^2}{d^2}\right]\right)$$

$$V^{e,h}_{\text{obl}}(r, z) = V^{e,h}_{\text{off}} \left(1 - \exp\left[-\frac{4(x^2 + y^2)}{d_x^2} - \frac{4z^2}{d_z^2}\right]\right)$$

FRET in single dense array of CdSe/ZnSe quantum dots





$$\frac{\mathrm{d}N_{\mathrm{d}}(E)}{\mathrm{d}t} = -N_{\mathrm{d}}(E)\left(\Gamma + \Gamma_{\mathrm{ET}}\right) + GN_{\mathrm{DOS}_1}(E) f_{\mathrm{d}}(E)$$

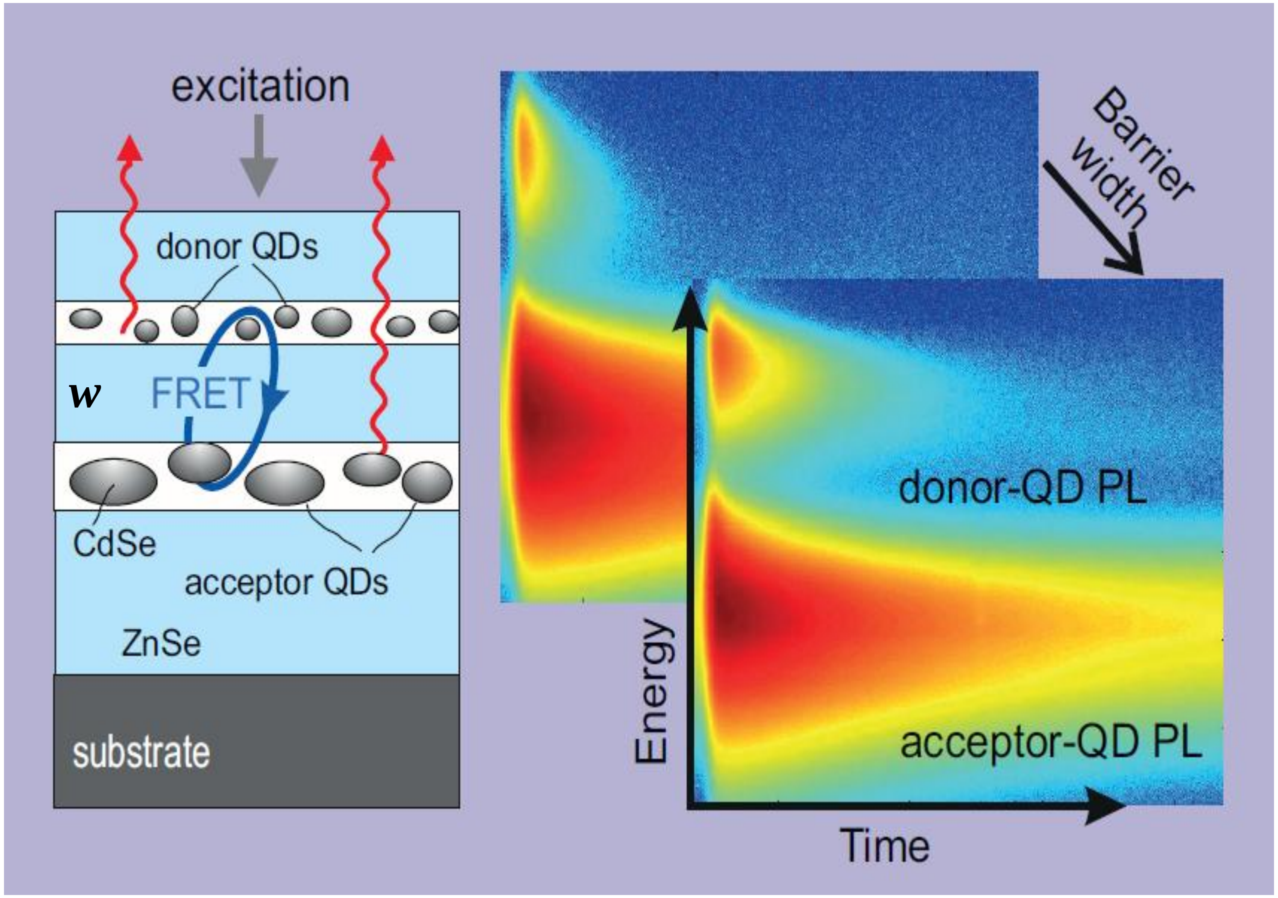
$$\frac{\mathrm{d}N_{\mathrm{i}}(E)}{\mathrm{d}t} = -N_{\mathrm{i}}(E)\Gamma + GN_{\mathrm{DOS}_1}(E)\left[1 - f_{\mathrm{d}}(E)\right]$$

$$\frac{\mathrm{d}N_{\mathrm{a}}(E)}{\mathrm{d}t} = -N_{\mathrm{a}}(E)\Gamma + \Gamma_{\mathrm{ET}} N_{\mathrm{d}}(E_{\mathrm{d}})$$

$$N_{\mathrm{DOS}_2}(E) = N_{\mathrm{DOS}_1}(E) - K_{\mathrm{ET}}\left(N_{\mathrm{DOS}_1}(E) f_{\mathrm{d}}(E) - N_{\mathrm{DOS}_1}(E_{\mathrm{d}}) f_{\mathrm{d}}(E_{\mathrm{d}})\right)$$

Energy transfer explains the narrow PL line

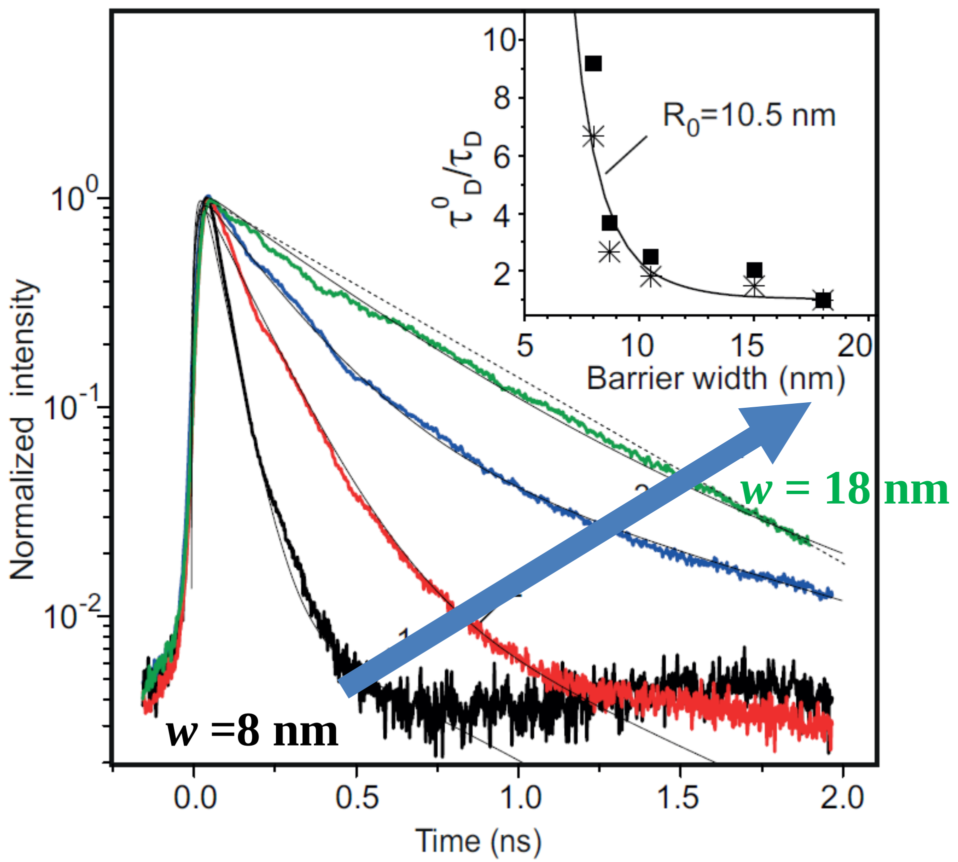
FRET between two arrays of CdSe/ZnSe quantum dots

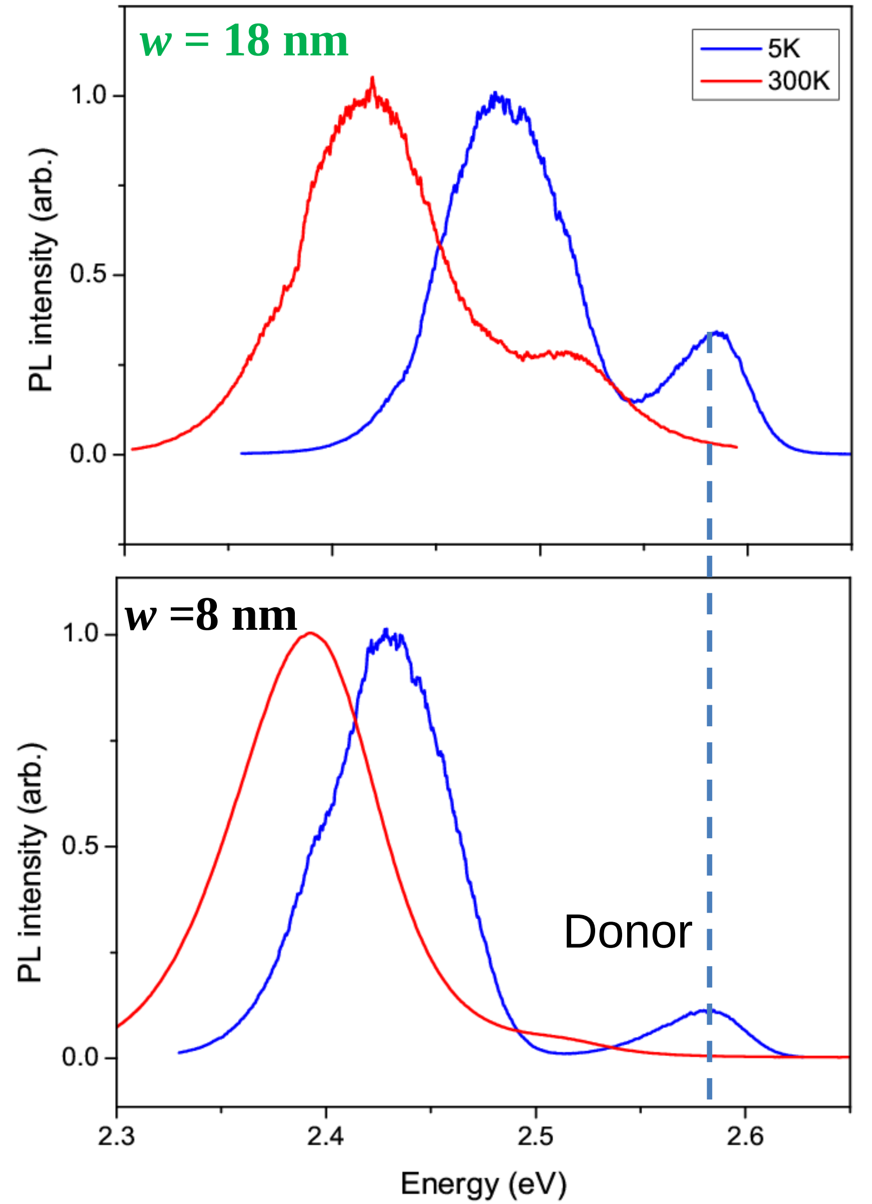


T.V. Shubina, G. Pozina, A.A. Toropov, Phys. Stat. Sol. B 1-7 (2016)

FRET between two arrays of CdSe/ZnSe quantum dots

T=5 K





$$I(t) = -I_{rise}e^{-t/t_{rise}} + I_1 e^{-t/t_1} + I_2 e^{-t/t_2}$$

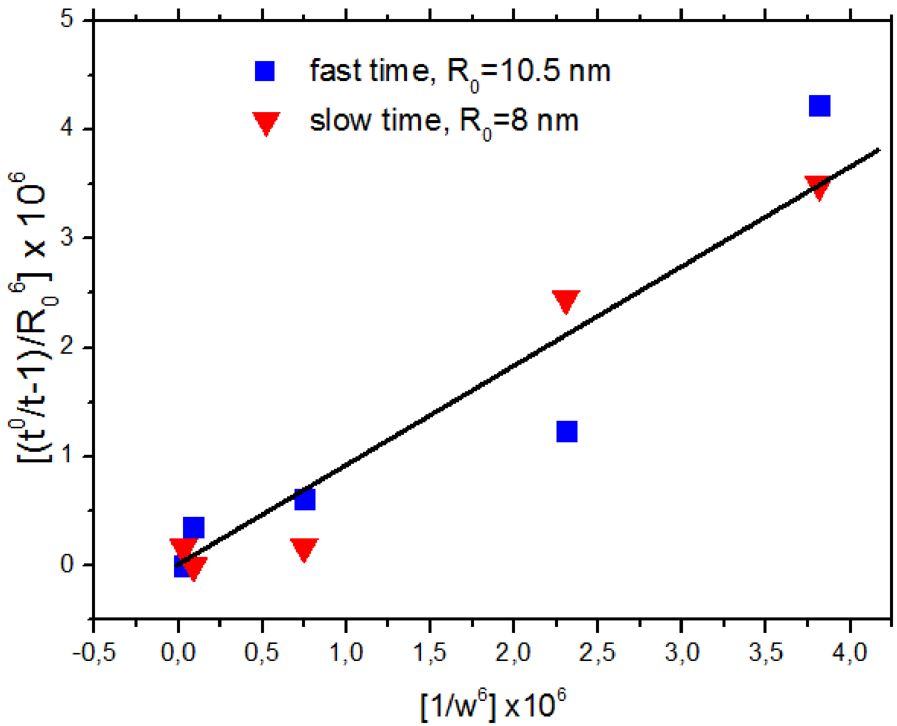
$\boldsymbol{R_{da}=w}$ $\quad\quad t^0/t = 1 + \left(R_0/R_{da}\right)^6$

ET Förster radius in arrays of CdSe/ZnSe quantum dots

T=5 K

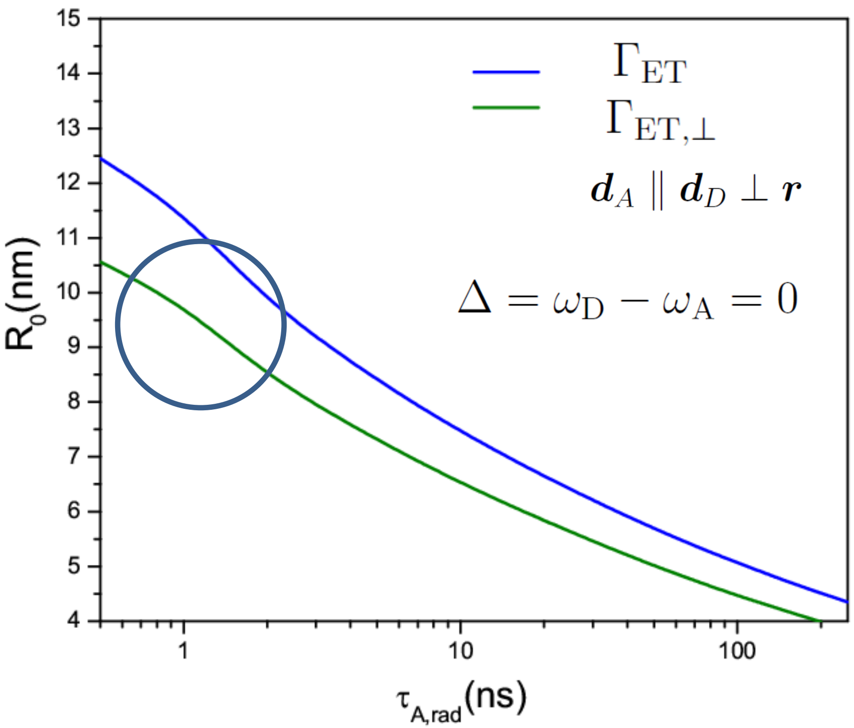
$$t^0/t = 1 + \left(R_0/R_{da}\right)^6$$

$\boldsymbol{R_{da}=w}$



Numerical results:

$\tau_A = 1$ ps, $E_D = \hbar\omega_D = 2.6$ eV



The exiton transfer is via the Förster resonance ET !
At low temperatures both bright and dark excitons participate in PL and ET ?

Summary

•The donor lifetime can be significantly modified only due to the nonradiative dipole-dipole Förster resonance energy transfer. ET efficiency depends on the acceptor characteristic times.

•At low temperature ET in ensemble of CdTe colloidal NCs is dominated by the FRET from dark exciton states. The dark exciton dipole momentum is caused by the admixture of the bright exciton and enhanced in magnetic field.

•The Förster resonance energy transfer in arrays of epitaxial CdSe/ZnSe quantum dots is demonstrated by time- and space-resolved photoluminescence spectroscopy. Probably both bright and dark exciton states are involved at low temperatures.